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INVESTIGATION OF SELECTED POTENTIAL ENVIRONMENTAL CONTAMINANTS

CHLORINATED PARAFFINS

SYRACUSE UNIVERSITY RESEARCH CORPORATION

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

NOVEMBER 1975

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This report reviews the potential environmental hazard from the commercial use of chlorinated paraffins. Chlorinated paraffins, in most cases, contain 10 to 30 carbon atoms and a chlorine content of 40 - 70%. They are used as lubricating oil additives, secondary plasticizers, and flame retardants. Information on physical and chemical properties, production methods and quantities, commercial uses and factors affecting environmental contamination, as well as information related to health and biological effects, are reviewed.

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N O T I C E

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Executive Summary

Commercial chlorinated paraffins are extremely complex mixtures that are similar in physical properties and commercial applications to the widely recognized environmental contaminant, polychlorinated biphenyls (PCB's). However, chlorinated paraffins are considerably less chemically stable relative to PCB's.

Approximately 74 million pounds of chlorinated paraffins were produced in the United States in 1973 and the market for these compounds continues to rise (>10% increase per year). Major applications of chlorinated paraffins include uses as lubricating oil additives (45% of total production), secondary vinyl plasticizers (24%), flame retardants in rubber, plastics, and paints (27%), and traffic paint additives (4%). Applications of PCB's as oil additives and plasticizers have been suggested as major sources of environmental contamination. However, the quantities of chlorinated paraffins released to the environment are unknown and there are no published monitoring data from which estimates could be made. The lack of monitoring data is directly attributable to the lack of a specific and sensitive analytical method. The best method presently being used is capable of measuring only 0.5 ppm and can only be used with certain commercial products. However, some monitoring data from Great Britan are expected to be published relatively soon, which use an analytical method that is sensitive to approximately 0.05 ppm. Conclusive studies have not been conducted to determine the environmental fate and persistence of the commercial formulations, although there is evidence that degradation occurs with some formulations, based upon oxygen consumption by microorganisms or loss of the parent compound. From the available information, it appears that chlorinated paraffins are probably less persistent than PCB's. No information is available on metabolites that

might be formed. The potential for bioaccumulation of chlorinated paraffins in fish appears to be quite small based upon experimental results, but the possibility of metabolite bioaccumulation has not been ruled out. Chlorinated paraffins exhibit a low degree of acute toxicity when administered by oral, dermal, or inhalational routes. However, lacking is any information on long term, low level exposures, although some preliminary subacute investigations with fish have produced significant mortality and numerous sub-lethal effects. These results suggest the value of exploring subacute effects in higher animals.

In summary, because of the limited data available, a conclusive environmental hazard assessment of chlorinated paraffins is not possible. No published monitoring data are available yet; the chemical structure, bioaccumulation potential, and toxicity of the environmental degradation products are unknown; and the available toxicity data on the commercial products are completely inadequate for assessing potential detrimental effects from trace contamination. However, from the available data, it can be concluded that chlorinated paraffins are (1) produced in larger quantities than PCB's, (2) are likely to be released to the environment, (3) are less mobile and persistent than PCB's, and (4) are less acutely toxic.

This report reviews commercially important chlorinated paraffins, which, in most cases, have 10 to 30 carbon atoms and a chlorine content of 40-70% (Hardie, 1964). Other chlorinated aliphatic compounds, such as chlorinated fatty acids, long-chained alcohols, alkylaromatic compounds, and polyethylene, are considered only when warranted by the available information.

I. Physical and Chemical Data

A. Structure and Properties

1. Chemical Structure

As the term implies, chlorinated paraffins are chlorinated derivatives of paraffinic hydrocarbons. In terms of the number of isomers, these formulations exceed such complicated commercial mixtures as polychlorinated biphenyls (PCB's) and chlorinated naphthalenes. This is due to the mixture of parent paraffinic hydrocarbons (usually various chain lengths) which are used commercially in the chlorination process. In contrast, only one parent hydrocarbon, i.e., biphenyl or naphthalene, is used with polychlorinated biphenyls and chlorinated naphthalenes, respectively.

In the United Kingdom, a distinction is made between chlorinated paraffins that are derived from liquid paraffins as opposed to those made from solid parent material, the latter being referred to as chlorinated-paraffin waxes (Hardie, 1964). In America, the term chlorinated paraffins refers to "chlorinated, mainly straight-chain, saturated hydrocarbons of the C_{10} - C_{30} range" (Hardie, 1964). The broader American term will be used in this review.

The commercial chlorinated paraffins are usually produced from a mixture of n-paraffins of varying chain lengths. This is illustrated by the

work of Zitko (1974b) and Panzel and Ballschmiter (1974). These investigators reductively dechlorinated some commercial chlorinated paraffins and then analyzed the resulting hydrocarbons by gas chromatography. Zitko's (1974b) results are depicted in Table 1 and Panzel and Ballschmiter's (1974) results are presented in Figure 1.

Table 1. Composition of Paraffins Obtained by Dechlorination of Different Chlorinated Paraffin Preparations (Zitko, 1974b)

	Percent							
Chlorinated Paraffin	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}
Chloroparaffin, 40%	4.5	10.0	15.7	19.3	18.5	15.3	9.8	6.7
Clorafin 40	3.7	8.2	14.0	17.5	19.2	17.4	12.4	7.6
CP 40	3.9	9.1	14.9	19.2	19.8	18.0	15.1	-
Cereclor 42	3.6	8.8	14.7	18.6	19.5	17.2	11.5	6.0
Chloroparaffin, 50%	7.4	14.9	20.7	23.1	19.9	14.0	-	-

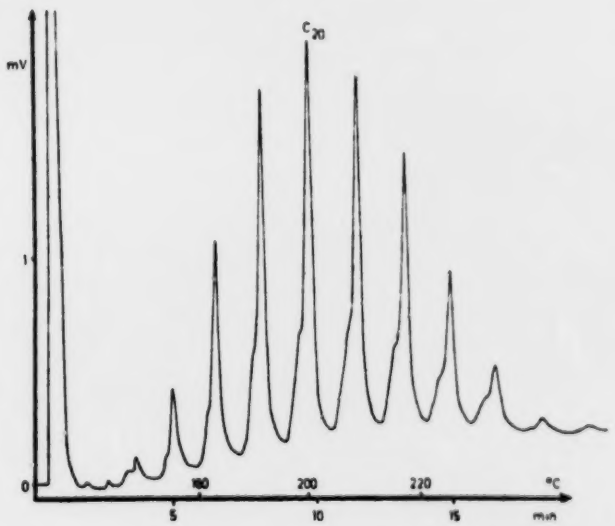

Figure 1. Gas Chromatograph of the Hydrocarbons Resulting from Reductive Dechlorination of CP44 (Panzel and Ballschmiter, 1974). Permission granted by Springer-Verlage.

The number and position of the substituted chlorines is dependent upon the amount of branching or other non-paraffinic structures in the parent hydrocarbon mixture and the extent of chlorination. The reactivity of aliphatic hydrogens during free-radical chlorination is dependent upon the acidity of the substituted hydrogen; the more acidic the less replaceable. Thus, tertiary carbons are chlorinated faster than secondary followed by primary (Bratolyubov, 1961). Since the paraffinic hydrocarbon mixtures used commercially contain mostly straight chained saturated hydrocarbons, secondary and primary carbons are primarily available. Therefore, the chlorines are probably randomly distributed, up to a point, along the methylene ($-CH_2-$) groups of the carbon chain. Two chlorines attached to the same carbon is unlikely, since the first chlorine substitution decreases the reactivity of the other hydrogens on the carbon attached to the chlorine. Table 2 illustrates this decrease in reactivity caused by the inductive effect of the chlorine atom. This inductive effect also inhibits vicinal substitution ($-\overset{Cl}{C}-\overset{Cl}{C}-$) whenever other sites of reaction are possible. As the commercial product approaches 70% chlorine, the chain will approach the condition where one atom of chlorine is attached to each carbon atom.

Table 2 . Effect of Chlorine Atom on Reactivity of Hydrogen Atoms in n-Butane (Bratolyubov, 1961)

Position of Cl atom	C_4 ——	C_3 ——	C_2 ——	C_1 —— Cl
% Substituted on chlorination	27	47	22	7
Relative Reactivity of H Atom	2.6	6.7	3.2	1

This distribution of chlorine along the paraffinic chain is supported by some experimental evidence. For example, chlorination of a C_{20} paraffin can be continued until the chlorine content is slightly more than 70% (i.e., $C_{20}H_{22}C\ell_{20}$); thereafter, chlorine can be introduced only with difficulty (Hardie, 1964). This corresponds to substitution of one chlorine on every carbon atom. Zitko and Arsenault (1974) noted that the lack of $CC\ell_2$ groups "was confirmed experimentally from NMR spectra of chlorinated paraffins with less than 60% chlorine (Gusev et al., 1968) and of chlorinated polyethylene (Heintke and Keller, 1971)". Heisele and Colelli (1965) have suggestive evidence that mixtures that are less than fully chlorinated contain all the statistically possible isomers. From a chlorinated nonane (99.7 mole percent) mixture, they were able to count all the 25 possible dichlorononane compounds, although the quantities of the isomers present varied greatly. Gas chromatography was used for determining the number of peaks, and the disubstituted structure was assigned by relative retention time on a non-polar column.

The chlorinated paraffins, besides containing various isomers of mono-, di-, trichloro-, etc. compounds, also contain various ratios of the mono-, di-, trichloro-, etc. compounds as well as unchlorinated paraffin. The relative ratios are dependent upon the degree of chlorination. The study by Heisele and Colelli (1965) measured by gas chromatography the amount of nonane and mono-, di-, and trichlorononane at various chlorination percentages. These results are noted in Table 3.

Table 3. Nonane Chlorination Distribution
(Heisele and Colelli, 1965)

	Chlorine Concentration (%)								
	3	6	12	17	21	29	35	42	48
Nonane	80	59	43	26	20	10	3	2	-
Mono	20	37	41	46	46	39	25	9	-
Di		4	16	26	30	41	47		
Tri				2*	4*	10*	28*		

* Estimate

Similar studies were reported by Koennecke and Hahn (1962) and Teubel et al. (1962), except that they separated the mixture into various fractions by chromatography on silica and used paraffins containing larger numbers of carbons. Their results are presented in Tables 4 and 5. From these studies, it can be seen that as the degree of chlorination approaches 50%, the amount of paraffin and monochlorinated paraffin becomes very small.

Table 4. Percent Distribution of Chlorinated Paraffins (C_{26})
at Different Degrees of Chlorination
(Koennecke and Hahn, 1962)

	Degree of Chlorination (wt% chlorine)							
	17.2	22.6	27.2	32.9	36.0	39.5	42.8	46.8
Paraffin (C_{26})	10.6	3.6	1.4	0.34	0.27	0.08	-	-
Monochloro-	27.3	14.5	7.8	1.8	0.7	0.6	0.1	-
Dichloro-	20.1	17.6	10.5	4.0	1.4	0.68	0.38	-
Polychloro-	40.6	63.0	79.4	93.1	96.5	97.9	98.9	99.1

Table 5 . Distribution of Chlorinated Paraffins
(Teubel et al., 1962)

mol. Cℓ/mol. paraffin	C_{19} 26% chlorine (vol%)	C_{20} - C_{30} 26.1% chlorine (vol%)
0	4.4	1.1
1	17.8	3.7
2	27.8	11.0
3	28.9	14.2
4	11.2	24.1
5	7.7	25.2
6	-	12.5
>6	-	8.2

Because the commercial chlorinated paraffins are made from commercial paraffin waxes, it is likely that non-n-paraffinic hydrocarbons, such as alicyclic and aromatic compounds, will be present in small amounts in the parent paraffin waxes. Chlorination of these materials may result in very unstable carbon-chlorine linkages, such as benzylic and tertiary carbon-chlorine bonds. Tertiary chlorines are very likely when isoparaffins are present, because tertiary carbons are chlorinated faster than primary or secondary. The order of stability of carbon-chlorine linkages is: primary Cℓ> secondary Cℓ> alicyclic Cℓ> benzylic Cℓ>, allylic Cℓ, tertiary Cℓ. Weintraub and Mottern (1965) have studied the relative amount of labile chlorine atoms in Chlorowax 40 and 70 by testing the chlorinated paraffins with silver nitrate reagent and weighing the silver chloride precipitate. Based partially on the data in Table 6, they concluded that "the labile chlorine was proportional to the oil and/or to the naphthenic (alicyclic) content of the wax, and inversely proportional to the total chlorine content."

Table 6. Effect of Total Chlorine and Oil Content on Percent Labile Chlorine (Weintraub and Mottern, 1965)

Wax (m.p., °F)	Oil (%)	Cl (Wt. %)	Labile Cl (Wt. %)
128	0.7	60.0	9.5
128	0.7	67.0	3.7
126	15.0	44.0	38.9
126	15.0	58.6	15.7
Chlorowax 40	<1.0	40	45.3
Chlorowax 70	<1.0	70	1.4

The high percentage of labile chlorine for Chlorowax 40 is difficult to explain. One possibility is that the initial dehydrochlorination produces allylic and benzylic chlorine atoms, and this perpetuates the instability. Inductive stability may be provided to tertiary chlorine atoms by vicinal chlorine atoms in the higher chlorinated materials, resulting in less labile chlorines in Chlorowax 70. Whatever the explanation, it appears that small amounts of tertiary, allylic, and/or benzylic chlorines are present in the commercial chlorinated paraffins.

In summary, commercial chlorinated paraffins are complex mixtures containing numerous isomers and varying numbers of chlorines per molecule. The starting hydrocarbon material usually contains mostly n-paraffins with varying numbers of carbon atoms (e.g., C_9 - C_{12} or C_{20} - C_{25}). However, some small amounts of isoparaffins or aromatics may be present. The highest chlorinated paraffins (approximately 70% chlorine by weight) roughly correspond to one chlorine atom substituted on each carbon atom.

2. Physical Properties of Commercial Materials

Because of the wide variety of starting paraffin mixtures and degrees of chlorination possible, the physical properties of the commercial chlorinated paraffins cover a broad range. Competitive formulations are grouped together and illustrated in Table 7. The properties having the most industrial significance are the viscous character (lubricant applications), non-flammability (flame retardant applications), relatively low toxicity, miscibility with plasticizers (secondary plasticizer applications), and the ability, at elevated temperatures, to split off small quantities of hydrogen chloride (extreme-pressure lubricant applications) (Hardie, 1964).

For any given paraffin feedstock, the viscosity and specific gravity increase with the chlorine content. Both liquid chlorinated paraffins as well as brittle, resinous solids are possible. Initially, as the chlorine content increases, the solidification point decreases as is illustrated in Figure 2. However, at a certain chlorine content, a point of inflection is reached and, thereafter, the solidification point increases with increasing chlorine content. The point of inflection will vary with different paraffin feedstocks.

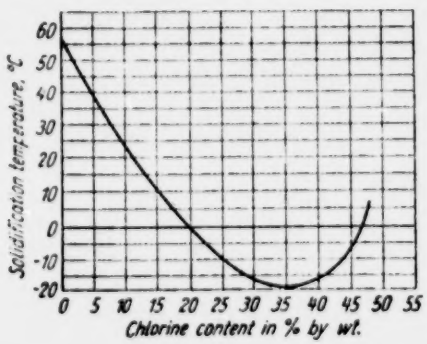

Figure 2. Solidification Temperature of Chloroparaffins as a Function of the Chlorine Content (Asinger, 1967) Permission granted by Pergamon Press Ltd.

Table 7. Physical Properties of Commercial Chlorinated Paraffins

Commercial Name	Company	Chlorine Content (wt%)	Average Chemical Formula	Average Molecular Weight	Viscosity Saybolt Univ. Seconds 100°F	210°F	Specific Gravity 25°C	Evaporation Rate g/cm²/hr. @100°C	Pour or Softening Point °C	Refractive Index	Heat Stability % HCl 4hr at 175°C
Paroil 140	Dover	42	$C_{22}H_{40}Cl_6$+	540	3,800	150	1.14	2.5×10^{-6}	0	1.50	0.4
Chlorowax 40	Diamond-Shamrock	43	$C_{24}H_{43}Cl_7$	560	4,000	150	1.17	60×10^{-6}	0	1.505	0.40
Chlorowax 43-150	"	43	-	-	4,000	150	1.17	-	-	-	-
CPF-0022	Pearsall	39-41	-	-	-	140-165	1.15-1.17	-	-	-	0.4
Clorafin 40	Hercules	-	-	-	-	-	-	-	-	-	-
Cereclor S-42	Imperial Chem. Ind. (ICI)	-	-	-	-	-	-	-	-	-	-
Unichlor 40	Neville	-	-	-	-	-	-	-	-	-	-
Chloroflo 40	Dover	37-38	$C_{20}H_{37}Cl_5$	455	600-660	52-65	1.07-1.10	80×10^{-6}	-30	1.467	0.4
Chlorowax LV	Diamond	39	-	460	1,050	80	1.120	80×10^{-6}	-20	1.501	0.25
Paroil 150-S	Dover	50-52	$C_{22}H_{36}Cl_8$	586	-	220-240	1.25	2.5×10^{-6}	15	1.490	0.5
Chlorowax 51-225	Diamond	51	-	-	14,000	225	1.27	-	-	-	-
Chlorowax 50	"	48	-	660	1.500	265	1.23	40×10^{-6}	10	1.516	0.4
Clorafin 50	Hercules	-	-	-	-	-	-	-	-	-	-
Cereclor LP 4985	I.C.I.	-	-	-	-	-	-	-	-	-	-
Cereclor L-51	I.C.I.	-	-	-	-	-	-	-	-	-	-
CW 300-50	Keil	50	-	588	20,000	300	1.25	-	-	-	0.2
CPF 0008	Pearsall	48-51	-	-	-	200-240	1.16-1.24	-	-	-	0.4
Paroil 1160	Dover	58-60	$C_{9-17}H_{14-24}Cl_{6-10}$	335-350	8,200-10,500	55-70	1.343	388×10^{-6}	0	1.489	0.4
Chlorowax 57-60	Diamond	57	-	-	1,600	60	1.33	-	-	-	-
Chlorowax 500	"	-	-	-	-	-	-	-	-	-	-
Kloro 6000	Keil	60	-	-	980	-	1.38	-	-	-	-
FLX 0012	Pearsall	58-61	-	-	-	65-75	1.33-1.39	-	-	-	0.20
Paroil 160	Dover	59	-	-	1,700	60	1.335	500×10^{-6}	-	1.489	0.3
Chlorowax 500-C	Diamond	59	$C_{12}H_{20}Cl_6$	415	1,500	65	1.35	-	-	1.516	0.20
C W 85-60	Keil	60	-	405	5,000	85	1.38	-	-	-	0.1
Unichlor 60-LV	Neville	-	-	-	-	-	-	-	-	-	-
Paroil 170HV	Dover	69-70	$C_{11}H_{15}Cl_9$	466	-	500-600	1.55	80×10^{-6}	40	1.53	0.5
Paroil 170-S	Dover	71-73	$C_{10}H_{12}Cl_{10}$	487	-	45-55	1.55	550×10^{-6}	-5	1.50	0.2
Diablo 700X	Diamond	69	-	-	4,500	75	-	-	-	-	-
Chlorez 700	Dover	69-72	$C_{20}H_{24}Cl_{18}$	903	-	-	1.7	1.5×10^{-6}	95-110	1.55	0.3
Chlorowax 70	Diamond	70	$C_{24}H_{28}Cl_{22}$	1,060	-	-	1.66	-	102	1.535	-
Cereclor 70	I.C.I.	70	$C_{23}H_{26}Cl_{22}$	-	-	-	1.63	-	85-90	-	-

As might be expected, the specific gravity increases as the average number of chlorine atoms per molecule increases. This correlation is frequently taken advantage of in order to provide rough estimates of the chlorine content.

The chlorinated paraffins have a "characteristic slight, and not unpleasant, odor" (Hardie, 1964). This is probably due to small quantities of lower molecular products, which provide small, but measurable vapor pressures. For example, the vapor pressure of a C_{23} paraffin chlorinated to 42, 48, or 54% was 2×10^{-5} mm Hg when measured at 65°C (Hardie, 1964). The industry routinely measures the volatility of their commercial products in terms of evaporation rate ($g/cm^2/hr$ at 100°C) (see Table 7).

The color of the commercial chlorinated paraffins is usually found in the yellow range, varying from light amber to pale yellow, honey, or yellow color. However, color is not a constant characteristic since it is dependent upon manufacturing (high temperatures increase the color) and subsequent storage conditions (Hardie, 1964).

As noted earlier, the solubility properties of chlorinated paraffins have considerable significance. None of the chlorinated paraffins are soluble in water or the lower alcohols (Hardie, 1964). However, many of the products can be emulsified with water (approximately 70/30 chlorinated paraffin to water) and are used in that form mostly for flame retardancy applications. The following formulations are water dispersions: Rez-O-Sperse A-1, 3, A-4 (Dover), Delvet 65, 65-S (Diamond-Shamrock) and Unichlor 70-65 (Neville).

Table 8 summarizes the solubility of various chlorinated paraffins in organic solvents and oils. Formulations containing over 40% chlorine are

compatible "with natural rubber, chlorinated rubber, synthetic rubber, polyester resins, and many alkyl resins, as well as with such common plasticizing compounds as dioctyl or dibutyl phthalate and tricresyl phosphate" (Hardie, 1964). This compatibility with common resins and plastics, especially polyvinylchloride, and with common plasticizers allows chlorinated paraffins to be used as plasticizer extenders (secondary plasticizer).

Table 8. Solubility of Chlorinated Paraffins
(Roberts, 1949; Hardie, 1964)

% Chlorine	
~28%	- Soluble in mineral and lubricating oils
42-54%	- Soluble in normal aliphatic and aromatic hydrocarbons, chlorinated solvents, and ether - Miscible with vegetable oils and mineral oils
~70%	- Soluble in vegetable and mineral oils, chlorinated solvents, esters, ketones, aromatic hydrocarbons, and terpenes - Insoluble in alcohols, aliphatic hydrocarbons, and ethers

3. Principal Contaminants

Because commercial chlorinated paraffins are extremely complex mixtures, it is difficult to distinguish between commonly occurring isomers and contaminants. For example, are the tertiary chlorine substituted products formed from isoparaffins contaminants or not? What about the heavy olefins formed during thermal dehydrohalogenation? Chlorinated aromatic impurities resulting from aromatics in the paraffin feed stock are somewhat more clear cut since they are certainly not paraffins. Zitko and Arsenault (1974) examined the ultraviolet spectra (absorbance at 275 mm) of Cereclor 42, Clorofin 40, and Chlorez 700 and concluded that the concentration of chlorinated aromatic hydrocarbons was probably not very high. Similarly, Ligezowa et al. (1974) used infrared spectrometry with a technical chlorinated paraffin (~26 C atoms) that had been separated by column chromatography to prove the absence of large amounts of unsaturated material.

During chlorinated paraffin manufacture, some chlorinated solvents are used to increase the rate of chlorination. This is especially true with high percentage chlorine products where the increase in viscosity due to added chlorine results in slow chlorination rates. Carbon tetrachloride is the most common solvent that is used, although hexachlorobutadiene has been reported (Hardie, 1964). Harnagea and Crisan (1974) have developed a rapid infrared spectrophotometric method for determining carbon tetrachloride in chlorinated paraffins containing 70% chlorine. Heisele and Colelli (1965) suggest that carbon tetrachloride as well as methylene chloride, chloroform, and perchloroethylene may be formed from cracking during chlorination. These materials may be found in trace amounts in the final product. It is unlikely that large amounts will remain following the hydrogen chloride removal step (see Section III-A-3, p. 27).

Chlorination catalysts are rarely used, although one process has reportedly used calcium oleate or benzoate (Hardie, 1964). Metal catalysts are avoided since they may promote decomposition of the chlorinated paraffins. The Diamond Shamrock Chemical Company has analyzed its Chlorowax product line for a number of metals by atomic absorption spectrometry. The analyses are presented in Table 9. It is unknown whether other product lines would have similar elemental concentrations.

Stabilizers are frequently added to chlorinated paraffins to inhibit decomposition, especially when the product is intended for elevated temperature use. Table 10 lists the compounds that have reportedly been used as stabilizers. Since the dehydrohalogenation process is not catalyzed by oxygen, antioxidants are not used as stabilizers. Other additives are combined with chlorinated paraffins to increase their flame retardancy (e.g., antimony oxide). These will be discussed in Section II-B, p. 32.

Table 9. Metal Analyses of Diamond Shamrock Chlorowax
Parts Per Million (ppm)

Element		Minimum Detection Limit "ppm"	Resinous CHLOROWAX 70 Average Detected "ppm"	Resinous CHLOROWAX 70 Maximum Detected "ppm"	Liquid All Grades Average Detected "ppm"	Liquid All Grades Maximum Detected "ppm"
Lead	Pb	0.002	0.01	0.02	0.02	0.04
Cadmium	Cd	0.040	(Less than	0.040)	(Less than	0.040)
Mercury	Hg	0.025	0.12	0.12	0.07	0.15
Chromium	Cr	0.001	0.07	0.12	0.01	0.02
Iron	Fe	0.006	0.88	1.14	0.94	1.65
Copper	Cu	0.001	0.02	0.03	0.02	0.10
Vanadium	V	0.080	(Less than	0.080)	(Less than	0.080)
Titanium	Ti	0.240	(Less than	0.240)	(Less than	0.240)
Calcium	Ca	0.150	1.35	2.0	1.08	2.50
Magnesium	Mg	0.025	0.17	0.23	0.08	0.24
Sodium	Na	0.050	0.76	0.80	0.92	2.10
Potassium	K	0.200	0.76	0.85	0.70	2.80
Barium	Ba	0.090	(Less than	0.090)	0.24	0.70
Silver	Ag	0.150	0.21	0.34	0.25	0.87
Cobalt	Co	2.00	(Less than	2.00)	(Less than	2.00)
Molybdenum	Mo	0.50	(Less than	0.50)	(Less than	0.50)
Bismuth	Bi	1.10	(Less than	1.10)	(Less than	1.10)
Aluminum	Al	0.50	1.1	1.2	1.0	1.25
Zinc	Zn	0.03	0.06	0.08	0.04	0.12
Tin	Sn	1.9	5.2	7.4	2.6	6.3
Antimony	Sb	1.6	5.3	6.5	3.0	9.5

Table 10. Stabilizers Used with Chlorinated Paraffins

Reference	Compounds
Roberts (1949)	Hydrocarbons of the terpene or pinene groups Triethanolamine Phenoxypropylene oxide Acrylated ethylenimines Ethylene oxide
Asinger (1967)	Lead oxide (about 10% added)
Hardie (1964)	Ethylene glycol 1,2- and 1,3-Dihydroxypropane Glycerol Pentaerythritol Organometallic compounds of tin Pyrimidine compounds 3-Phenoxy-1,2-epoxypropane Certain compounds of lead or cadmium Phosphates Propylene glycol
Compagnie Francaise de Raffinage (1972)	Ethylenediaminetetraacetic acid (EDTA) di-Na EDTA Nitrilotriacetic acid Poly (4-vinylpyridine) Isoquinoline
Hirashima & Miyasaki (1972)	Acetonitrile
Krockenberger (1972)	Alkanediol diglycidyl ethers
Nishimura *et al*, (1972)	Alkaline earth hydroxide

B. Chemistry

1. Reactions Involved in Uses

There are three major applications of chlorinated paraffins: (1) as a secondary plasticizer, (2) as a lubricant and cutting fluid additive, and (3) as a flame retardant. The last two applications depend upon the ability of chlorinated paraffins to release hydrochloric acid at elevated temperatures. Actually, the thermal stability of chlorinated paraffins at normal processing temperatures is quite high. The conventional industrial test for heat stability consists of heating the sample to 347°F (175°C) for 4 hours and measuring the liberated hydrogen chloride. Results from this test for various formulations are presented in Table 7. In all the formulations noted, less than 0.5% HCℓ is liberated. However, at elevated temperatures or by adding accelerators (e.g., iron oxides, zinc oxides, zinc carbonates and zinc borates, Scheer, 1944), the decomposition process is considerably increased. Above 300°C dehydrochlorination is rapid and intense blackening occurs (Hardie, 1964). This release of hydrochloric acid can be used in two ways: (1) to react with metal surfaces to form a thin but strong solid film of metal chloride lubricant (chlorides also make the material act more brittle which is advantageous for cutting) (Matthijsen and Van Den Brekel, 1967) or (2) to inhibit the radical reactions in a flame.

In contrast to lubrication and flame retardancy uses, many applications depend upon the stability of chlorinated paraffins at lower temperatures. For example, if the material is to be used as a secondary plasticizer, it should not decompose and turn black during the processing of

the plastic (thermal molding is frequently used). Dehydrochlorination of chlorinated paraffins is accelerated by hydrogen chloride, zinc, tin, and antimony chloride "which indicates that it proceeds by an ionic mechanism" (Zitko and Arsenault, 1974). Stabilizers, which are added to chlorinated paraffin formulations, are based upon disruption of the decomposition reaction. Thus, the stabilizers listed in Table 10 attempt to bind the hydrochloric acid or complex the possible metal catalyst contaminants. Weintraub and Mottern (1965) have suggested that the amount of hydrogen chloride evolved during the thermal stability test at 175°C is proportional to the non-n-paraffinic content of the starting hydrocarbon mixture.

2. Hydrolysis

Under ambient and neutral conditions, chlorinated paraffins appear to hydrolyze very slowly. In fact, many formulations consist of water emulsions of chlorinated paraffins. However, under pressure, and with aqueous or alcoholic alkali, dehydrochlorination takes place accompanied by polymerization (Hardie, 1964). Replacement of chlorines by hydroxyl groups has only been reported at elevated temperatures using alkali and alkaline earth hydroxides (Hardie, 1964). Roberts (1949) has reported that chlorinated unsaturated alcohols have been prepared from chlorinated paraffins by treatment with aqueous alkali metal hydroxides or carbonates under pressure with heating.

3. Oxidation

Oxygen apparently has no catalytic effect on the decomposition of chlorinated paraffins (Roberts, 1949). The substances are highly resistant

to oxidizing agents and antioxidants are of no value as stabilizers. Possible products from oxidation at elevated temperatures have not been determined.

4. Photolysis

Information on the photochemistry of chlorinated paraffins is somewhat contradictory. It has long been known that chlorinated paraffins exposed to direct sunlight will decompose at ordinary temperatures and evolve hydrogen chloride (Roberts, 1949; Hardie, 1964). This may be due to small amounts of impurities in the commercial product. In fact, formulations containing substantial quantities of branched-chain paraffins (allowing formation of unstable tertiary chlorides) may show unusually low light stability (Hardie, 1964).

However, the chlorinated paraffins must exhibit considerable photochemical stability since they are usually manufactured in the presence of light. Friedman and Lombardo (1975) have taken advantage of this relative photolytic stability to eliminate chlorinated aromatic interferences during analysis (see Section II-E, p. 62). They felt that since chlorinated paraffins are poor absorbers of UV irradiation, the substances should not undergo appreciable photochemical decomposition. They photolyzed a variety of chlorinated paraffins (Chlorowax 500, Unichlor 70LV, Cereclor S-45 and S-52) in petroleum ether using high energy light (13% of the light energy was in the 220-280 nm region). No decompostion was noted. Although these conditions are considerably different than sunlight (>290 nm) irradiation of the concentrated chlorinated paraffin, it is unlikely that a substance that does not photodegrade under high energy light will degrade under lower energy light, especially since the high energy light contains wavelengths comparable to lower energy light. Thus, it appears that chlorinated paraffins do not photodegrade, although in the concentrated form, some decomposition may be noted (increased color and hydrogen chloride evolution) probably due to small amounts of contaminants.

5. Other

Information on other chemical reactions of chlorinated paraffins is very limited. Hardie (1964) states that chlorinated paraffins will condense with aromatic compounds such as benzene, toluene, xylenes, naphthalenes, and phenol in the presence of anhydrous aluminum chloride. Paraflow, a pour-point depressant, is produced in this manner by Friedel-Crafts condensation of a chlorinated paraffin (10-12% Cℓ) with naphthalene (Roberts, 1949). Addition of Paraflow to lubricating oils reduces the pour-point, making the lubricant suitable for low temperature applications (Scheer, 1944).

Both Zitko (1974b) and Panzel and Ballschmiter (1974) have used the reductive dechlorination by sodium bis(2-methoxyethoxy)aluminum hydride as a confirmatory analytical technique for chlorinated paraffins. The hydride usually reacts with aliphatic and aromatic organohalogen compounds to yield the parent hydrocarbons for monosubstituted alkanes and the respective alkenes for the vicinally disubstituted alkanes. Typical reaction yields from hydride reduction of commercial chlorinated paraffin preparations are indicated in Table 11. Unexpectedly, hydroxyl olefins were isolated in the reduced product. Zitko (1974b) suggests that the hydroxyl groups may be due to addition of water to the double bonds formed by chlorine elimination from vicinal carbon atoms.

Table 11. Product Yields From Reductive Dechlorination of Commercial Chlorinated Paraffin Products (Zitko, 1974b)

Formulation	Parent Hydrocarbons (%)	Hydroxyl Olefin (%)
Chloroparaffin (40% Cℓ)	20.8	
C P 40	16.0	
Clorafin 40 (preparative run)	40	22
Cereclor 42	37.0	
Chloroparaffin (50% Cℓ)	9.0	
Chlorez 700	not detectable	75

II. Environmental Exposure Factors

A. Production and Consumption

1. Quantity Produced

The liquid chlorinated paraffins were first used in sizable quantities during World War I. They were used as a solvent for Dichloroamine T in antiseptic nasal and throat sprays (Scheer, 1944). In 1932, the incorporation of chlorinated paraffins as an extreme pressure additive in lubricants provided the first large volume commercial use of chlorinated paraffins. However, the largest expansion in chlorinated paraffin production occurred during World War II. According to the U.S. Tariff Commission, the production in 1945 amounted to 50 million pounds, mostly due to the increase in use for weather and flameproofing of tent fabrics and camouflage netting (Roberts, 1949). Hardie (1964) noted that the output of chlorinated paraffins from January 1, 1944, to June 30, 1945, amounted to 63 million pounds. However, after the war production fell drastically, reaching approximately 14 million pounds by 1946. In the following years the production of chlorinated paraffins slowly increased, as is noted in Table 12, until it presently exceeds wartime production by about 25 million pounds.

Information on world production of chlorinated paraffins is not very plentiful or exact. Hardie (1964) reports an established world production of 75-100 million pounds for 1961 based upon natural and synthetic raw materials. This is approximately two to three times the U.S. production for that year.

Table 12. United States Chlorinated Paraffin Production and Sales (Hardie, 1964; U.S. Tariff Commission, 1959-1973)

	Production (10^3lbs.)			Sales (10^3lbs.)		
	Total	35-64%	All others	Total	35-64%	All others
1955	34,522			34,982		
1956	52,846			43,087		
1957	46,619			37,628		
1958	26,930			23,485		
1959	32,607	15,791	16,816	30,052	14,550	15,502
1960	34,583	25,989	8,594	34,471	26,009	8,462
1961	37,363	28,453	8,910	36,424	27,621	8,803
1962	39,712	30,113	9,599	37,980	29,441	8,539
1963	37,939	28,868	9,071	37,764	28,646	9,118
1964	39,887	29,664	10,223	- - -	- - -	- - -
1965	43,750	- - -	- - -	43,635	- - -	- - -
1966	60,051	- - -	- - -	60,734	- - -	- - -
1967	56,693	- - -	- - -	54,596	- - -	- - -
1968	57,607	- - -	- - -	58,780	- - -	- - -
1969	61,935	- - -	- - -	59,124	- - -	- - -
1970	58,371	35,393	22,978	56,913	34,612	22,301
1971	57,696	43,644	14,052	60,150	46,019	14,131
1972	63,453	48,806	14,647	65,238	50,181	15,057
1973	74,566	56,627	17,938	76,003	58,857	17,146

2. Producers, Major Distributors, Importers, Sources of Imports and Production Sites

In the United States, there are eight producers of chlorinated paraffins. These companies along with their plant locations and reported capacities are listed in Table 13. New capacities that have been announced are included in Table 13. The capacities noted are extremely flexible and, therefore, show only relative market positions of the various companies. Negotiations have been reported between Ansul Corp. and ICC Industries, Inc., of New York for the sale of Ansul's $5 million chlorinated paraffins business (Anon., 1974b).

Many of these producers have been manufacturing chlorinated paraffins for a considerable number of years. This is reflected in Table 14, which lists the producers of chlorinated paraffins during 1959-1974. Hooker Chemical Corporation has a plant in Niagara Falls, N.Y., with a rate capacity of 10 million pounds per year (Chemical Marketing Reporter, 1969), but for the last couple of years the company has only been producing chlorinated paraffins containing less than 35% chlorine, and recent references do not list the company as a producer (Dover Chemical Co., no date, a; SRI, 1974, 1975).

Table 15 lists the names and addresses of chlorinated paraffin suppliers. Many of the suppliers are known producers.

Imports of chlorinated paraffins are considered to be negligible. During 1964-67, the average total imports of chlorinated paraffins, chloromethane, 3-chloropropene, 1,1,1-trichloroethane, and other chlorinated hydrocarbons were 300,000 pounds (U.S. Tariff Commission, 1969).

Table 13. Capacities, Major Producers, and Sites of Production of Chlorinated Paraffins

Company	Site	Capacity ($X 10^6$ lbs.) 1975 SRI, 1974 1975	1975 Dover Chemical Corp. (no date a)	1976
The Ansul Corp.				
Dover Chem. Corp. (subsid.)	Dover, Ohio	26	26	26
Ferro Corp.				
Keil Chem Div.	Hammond, Ind.	26	25	25
Diamond-Shamrock Corp.***				
Diamond-Shamrock Chem. Co.				
Electro-Chem. Div.	Painesville, Ohio	18	22	22
I.C.I. United States, Inc.				
Plastics Div.	Bayonne, N.J.	10	10	10
Pearsall Chemical Co.	Phillipsburg, N.J.	5	9	9*
	LaPorte, Texas			12
Hercules, Inc.				
Coatings and Specialty				
Products Dept.	Parlin, N.J.	5	5	5
Neville Chem. Co.				
Chlorinated Prod. Div.	Sante Fe Springs, Ca.	5	5	10**
	Neville Island, Pa.			
Plastifax, Inc.	Gulfport, Miss.		1	1
	TOTAL	95	103	120

* Anon. (1975a)

** Anon. (1974a)

*** The Diamond Shamrock Corporation has announced plans for a 90 million lb. per-year chlorinated paraffins plant near Houston, Texas. The new plant is scheduled to be operating in late 1977 (Anon., 1975e).

Table 14. Producers of Chlorinated Paraffin During 1959-1974 (U.S. Tariff Commission 1959-1973)

	D.A.		H.K.	H.P.C.	U.C.P.	U.W.S.	C.C.H.	D.V.C.	W.O.I.-N.E.V.		E.N.J.	K.E.I.	K.P.S.		I.C.I.	Plastifax Inc.
	Diamond Alkali Co.	Diamond Shamrock Corp.	Hooker Chem. Corp.	Hercules Inc.	Union Carbide Plastics Co. Div.	Universal Western Chem. Co.	(Clinton Chem. Co.) After 1961 Pearsall Chem. Co.	Dover Chem. Co., 1974 Div. of Ansul	Western Organics Chem. Corp.	1967 Neville Chem. Co., Chlorinated Products Div.	Enjay Chem. Co., Div. of Humble Oil & Refining Co.	Keil Chem. Co., Div. of Ferro Corp.	Koppers Chem. & Dyestuffs Div.	K.P.C.-K.P.I. Pittsburgh Co. Tar Products Div.	I.C.I. Organics Inc.	
1959	X		X	X	X	X										
1960	X		X	X		X	X	X	X							
1961	X		X	X			X	X	X				X			
1962	X		X	X			X	X	X					X		
1963	X		X	X			X	X	X		X			X		
1964	X		X	X			X	X	X					X		
1965	X		X	X			X	X	X					X		
1966	X		X	X			X	X	X					X		
1967		X	X	X			X	X	X			X	X	X		
1968		X	X	X			X	X		X			X			
1969		X	X	X			X	X		X			X		X	
1970		X	X	X			X	X		X			X		X	
1971		X	X	X			X	X		X			X		X	
1972		X	X	X			X	X		X			X		X	
1973		X	X	X			X	X		X					X	
1974		X		X			X	X		X		X			X	X

* S.R.I., 1974, 1975; Dover Chem. Corp. (no date, a)

† only less than 35% Cl

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Table 15. Chlorinated Paraffin Distributors
(Chemical Marketing Reporter, 1974)

Company	Location
Agvar Chemicals, Inc.	New York, New York
Amoco Solvents & Chemicals Co.	Lakeview, California
Cron Chemical Corp. *	Houston, Texas
Diamond Shamrock Chemical Co. *	Cleveland, Ohio
Electro Chemicals Division *	
Dover Chemical Corp.	Dover, Ohio
ICI America Inc. *	Wilmington, Delaware
Intsel Corp.	New York, New York
Keil Chemical Co., Inc. *	Hammond, Indiana
Neville Chemical Co.,	Pittsburgh, Pennsylvania
Chlorinated Prod. Div. *	Santa Fe Springs, California
O'Connor-Boyles Chemicals, Inc.	Southfield, Michigan
Ohio Solvents & Chemicals Co.	Cleveland, Ohio
Pearsall Chemical Corp.	Phillipsburg, New Jersey
Plastifax, Inc. *	Gulfport, Mississippi
Sea Land Chemical Co.	Cleveland, Ohio
Stanalchem, Inc.	New York, New York
Stevenson Brothers & Co., Inc.	Philadelphia, Pennsylvania
Thompson-Hayward Chemical Co.	Kansas City, Kansas
E.F. Whitmore & Co.	San Marino, California

* Noted producers

3. Production Methods and Processes

Chlorinated paraffins are manufactured by liquid phase chlorination with chlorine gas at a temperature at which the viscosity of the paraffin is sufficiently low to allow rapid chlorination and hydrogen chloride evolution and at which decomposition of the product is not extensive (Hardie, 1964). Depending upon the paraffin feed stock, the temperature may range from 50° to 150°C, and the reaction is sometimes carried out at elevated pressures (15-100 psig) (Sittig, 1968). As the chlorine content in the product increases, it becomes so thick that chlorination above approximately 54% (Roberts, 1949) becomes slow and difficult. To decrease the viscosity and increase the chlorination rate, a solvent is usually added, and thus the highly chlorinated products are frequently produced by chlorination with solvent under reflux. Carbon tetrachloride is the most frequently used solvent, but other solvents such as hexachlorobutadiene have been reported (Hardie, 1964).

Configurations of the production plant may vary considerably. Both batch and continuous reactors can be used, although the continuous reactors usually consist of batch reactors in series. The reaction is exothermic so the reactor must be cooled. Since chlorination is a radical reaction, the reaction can be catalyzed by UV light or by radical initiators (e.g. azodiisobutyronitrile) (Zitko and Arsenault, 1974).

The flow diagram in Figure 3 is typical of a three stage operation consisting of three combined reactors and disengaging tank units which are so positioned that the chlorinated material will flow countercurrent to the flow of chlorine gas (25, 20, and 15 in Figure 3). In this

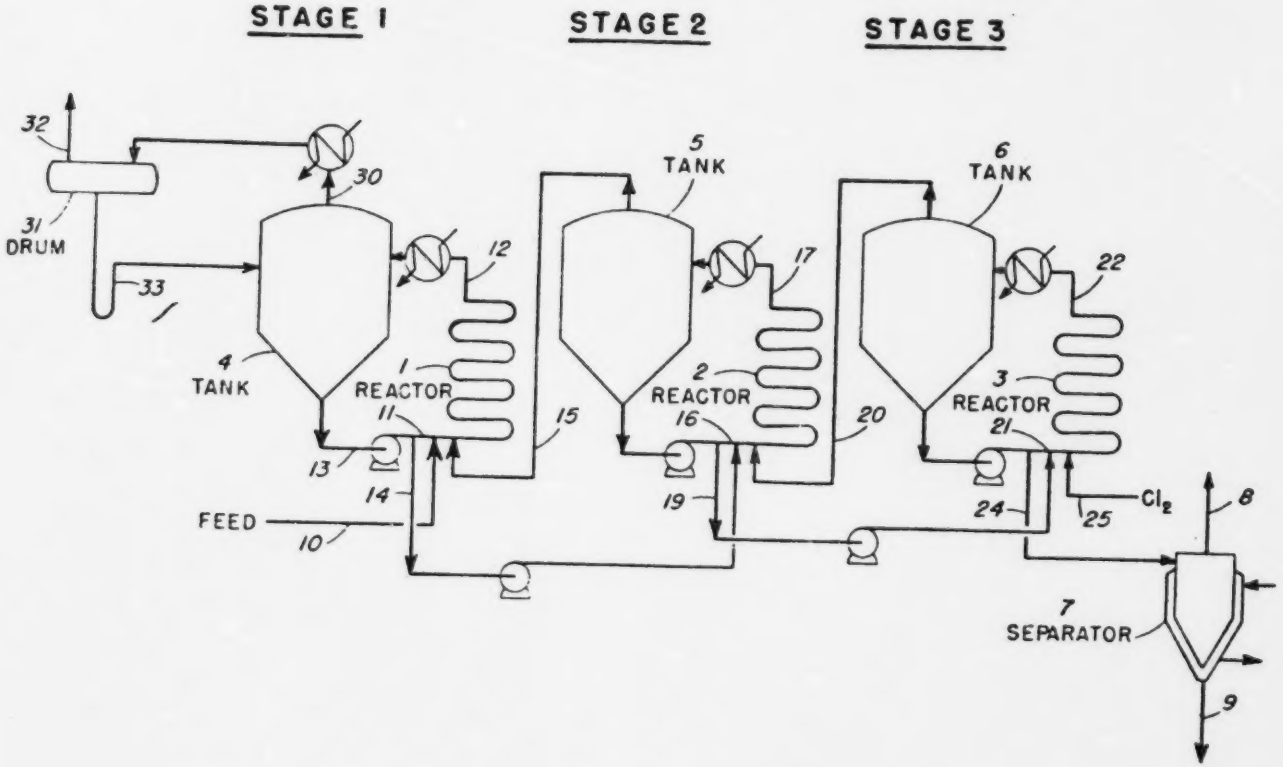

Figure 3. Process Plant for the Chlorination of Paraffin Wax (U.S. Patent 2,997,508 from Sittig, 1968)

three stage reactor, progressive stages of chlorination are accomplished. For example, the weight percent of chlorine in the chlorinated paraffin product withdrawn via lines 14, 19, and 24 are 22%, 45%, and 58%, respectively. The final chlorinated paraffin product is separated from the chlorine gas and hydrogen chloride by-product by blowing air or sometimes nitrogen or carbon dioxide (Scheer, 1944, Roberts, 1949, Sittig, 1968) through the product. Following removal of residual chlorine and hydrogen chloride, and solvent with the higher chlorinated paraffins, the product is stabilized.

4. Market Prices

The price of chlorinated paraffins can be a very important factor in determining whether these materials are used in various applications. This is especially true for secondary plasticizer applications where price may be an overriding factor (see Section II-B, p. 32). Figure 4 illustrates the relatively steady price history of chlorinated paraffins. For comparison purposes, the price history of di-2-ethylhexylphthalate (DEHP), one of the most widely used primary plasticizers, has also been plotted.

In 1973 the sales value of chlorinated paraffins totalled approximately $11.5 million. The chlorinated paraffins containing 35-64% chlorine totalled $7.9 million.

5. Market Trends

As Table 12 demonstrates, the production and sales of chlorinated paraffins have been on a steady increase. During the ten year period from 1963 to 1973, production has almost doubled (annual growth rate of approximately 7 per cent for the ten year period), but most of the growth occurred in 1963-66 and 1971-73. This is also reflected in the increase in the plant capacities. The capacity will be well over 100 million pounds per

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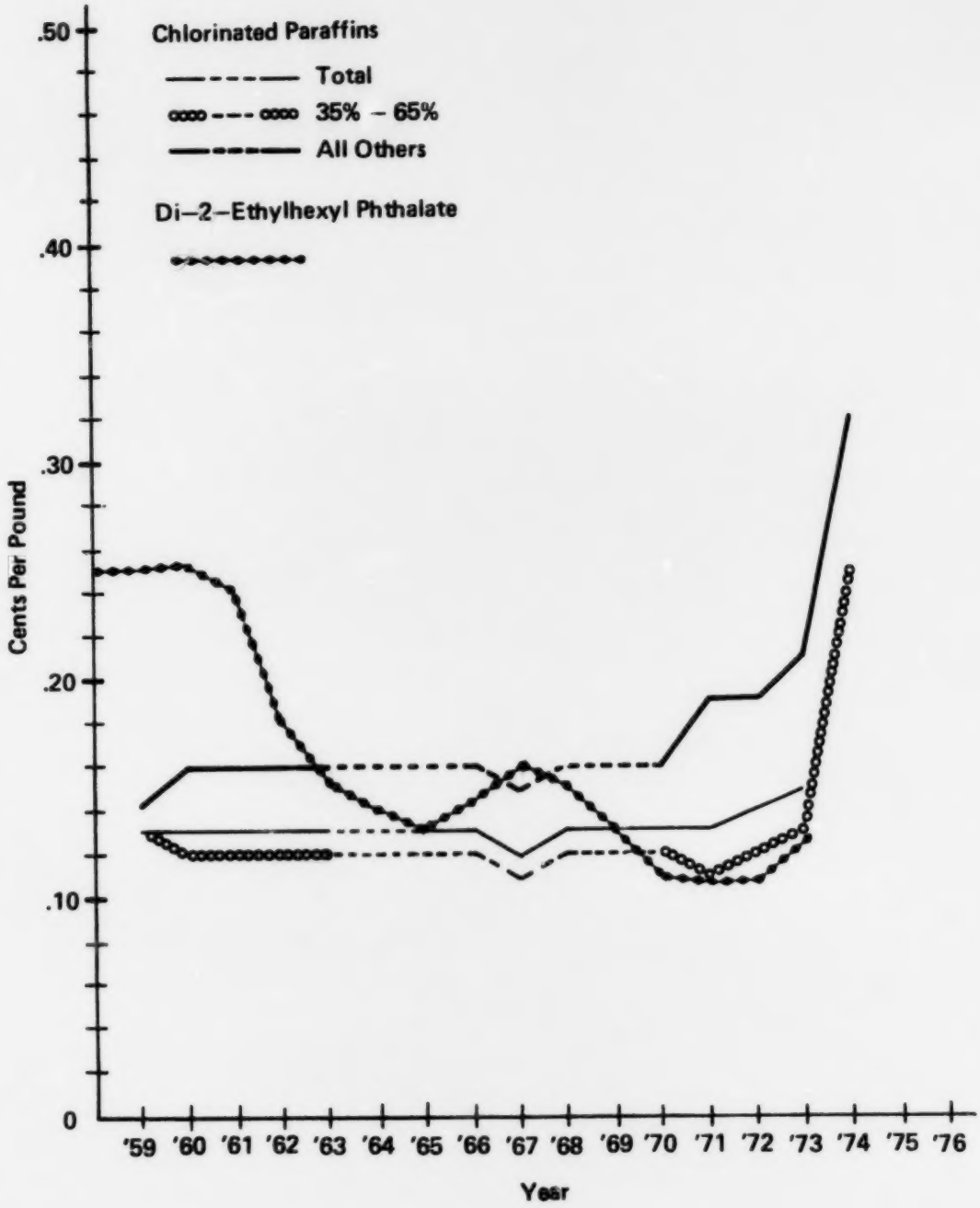


Figure 4. Average Unit Price/Lb. of Chlorinated Paraffins (U.S. Tariff Commission, 1959-1973;1974-Dover Chemical Corp. (no date a)

year in 1976 and has grown from 50 million in 1965 (Chemical Marketing Reporter, 1965), to 69 million in 1968 and 1969 (Chemical Marketing Reporter, 1968, 1969) and 95 million in 1974-75 (SRI, 1974, 1975).

The three major applications of chlorinated paraffins are lubricating and cutting oil additives (~45%), secondary plasticizers (24%), and flame retardancy uses in paint, rubber, and plastics (27%) (see Section II-B, p. 32). The market for oil additives seems to have matured and industrial sources suggest that the growth will probably not exceed 5% per year. In contrast, flame retardancy applications appear to have a bright future mostly due to growing public awareness and legislative requirements governing flame retardancy. Industrial sources suggest a possible growth rate of chlorinated paraffins for this application of approximately 35% per year. Other marketing surveys seem to confirm this optimism. Frost and Sullivan, Inc. (1975) suggest that the flame retardant market will double by 1978, and a spokesman for U.S. Industrial Chemicals Company estimated that the market for flame retardant plastics will grow at an average annual rate of 13 to 15% (Anon., 1975b). The market for secondary plasticizer applications is less defined, because the price of primary plasticizers has become more competitive. However, in cases where less chlorinated paraffin is required than the primary plasticizer that is replaced or where flame retardancy is a desirable asset, chlorinated paraffins will continue to be used as secondary plasticizers. Thus, overall it is likely that the market for chlorinated paraffins will continue to grow at a considerable rate.

B. Uses

1. Major Uses

Information on the quantities of chlorinated paraffins used in various applications is not very exact. However, the major applications appear to be as oil additives (~45%), as secondary plasticizers (~24%), and as flame retardant additives (~27%).

The first large commercial use of chlorinated paraffins was during World War II. At that time, these materials were selected as impregnating compositions "for treating canvas duck, camouflage nets and strips and other textiles materials to make them flame resistant, waterproof and mildewproof" (Scheer, 1944). Fabrics that were treated included cotton duck and burlap, jute, and osnaburg strips. Presently, textile applications are only a small part of the chlorinated paraffin market because they are not as resistant as other flame retardants [e.g., tetrakis (hydroxymethyl)phosphonium chloride] to washing and dry cleaning (Noble, 1974). Drake (1966) noted that the chlorinated paraffin - antimony oxide flame retardant finish is "more suitable for use on very heavy fabrics such as tents, tarpaulins, awnings, etc., and is not suitable for use on clothing, interior decorations, and the like". A small amount of chlorinated paraffins is still used for military applications, such as with tents (Noble, 1974).

Table 16 presents a breakdown of chlorinated paraffin applications for 1965-1973. Some trends are apparent from the data, but the difference between the 1973 figures and 1965, 1968, and 1969 figures is probably more attributable to the different sources of the information rather than particular trends.

Table 16. Major Applications of Chlorinated Paraffins

	Percentage of Total Market			
	1965*	1968*	1969*	1973**
Lubricating Oil Additives	65	35	35	45
Cutting & Drawing Oils	45			
Other Lube Uses	20			
Secondary Vinyl Plasticizer	20	35	35	24
Miscellaneous Solvent and Plasticizer (mostly flame retardancy uses)	15	20	20	27
Resinous Material for Coatings and Industrial Use		10	10	
Traffic Paints				4

* Chemical Marketing Reporter, 1965, 1968, 1969

* * Industry Sources

Oil additive applications are still a major portion of the total market, although their share has declined since the 1960's. This decline will probably continue since the oil additives market is considered to be relatively mature compared to the other applications.

Chlorinated paraffins are added to lubricating oils because of their viscous nature, their compatibility with oils, and gradual liberation of hydrogen chloride at elevated temperatures (Hardie, 1964). For the most part, only the liquid chlorinated paraffins are used. Chlorinated paraffins can provide both boundary lubrication (physical film formed) and extreme pressure activity (chemical reaction involved). If only extreme pressure activity is desired, a lower molecular weight or lower viscosity product is suitable and more economical. Chlorinated paraffins function as extreme pressure additives by slowly decomposing at elevated temperatures found near cutting surfaces or other

surfaces requiring lubrication to yield hydrogen chloride. The hydrogen chloride reacts with the metal surface and with the tool surface (in cutting oils). The reaction provides a high-melting, inorganic (iron chlorides) lubricant film on the metal surface which prevents massive welding and breakdown (Lee and Booser, 1967). With cutting oils, this results in a decrease of the cutting force, an increase in tool life, improved surface roughness, and smaller errors in dimensioning (Matthijsen and Van Den Brekel, 1967). When additional boundary lubrication is required, only the higher molecular weight, higher viscosity products can be used because of their greater film strength (Keil and Thompson, 1969). Typical formulations for cutting and extreme pressure applications are presented in Table 17. Added incentives for using chlorinated paraffins as oil additives are: (1) their relatively low cost as a source of chloride and (2) their ability to prevent corrosion, especially in low carbon steels.

Chlorinated paraffins are also used in drawing and stamping compounds. The high viscosity products, which are most frequently used, can be applied straight or diluted to a broad range of concentrations (Keil and Thompson, 1969).

Keil and Thompson (1969) conclude that chlorinated paraffins used as cutting fluids and drawing and stamping compounds are "highly effective, light in color and relatively free from smoking and gumming compared to metal-working fluids based on sulfurized fats".

Derivatives of chlorinated paraffins are also sometimes used as oil additives. Paraflow, a product made by reacting a 14% chlorine containing chlorinated paraffin with naphthalene, has been used as a pour-point depressant for lubricating oils (Hardie, 1964; Scheer, 1944; Roberts, 1949; Michel, 1968). Also, although more expensive, excellent lubricants are

Table 17. Formulations of Chlorinated Paraffins for Cutting and Extreme Pressure Oils (Keil and Thompson, 1969)

Chlorinated Paraffin	%	Application
Cutting Oils		
Low or High Viscosity	3-10	General purpose for ferrous and non-ferrous
High Viscosity	5-15	Heavy duty, low speed, metal gouging
Low Viscosity	5-15	Surface grinding oils (high alloy steels)
Extreme Pressure Soluble Oils		
Low Viscosity	5-10	General purpose for ferrous and non-ferrous
Low Viscosity	5-15	Surface grinding solubles (high alloy steels)
High Viscosity	20	Heavy duty E.P. solubles

provided by condensing C_{20} - C_{25} chlorinated paraffins with benzene, toluene, or the xylenes.

The other two major applications, use as a secondary plasticizer and as a flame retardant, are approximately equal in volume but frequently overlap. For example, chlorinated paraffins used as secondary plasticizers in polyvinyl chloride (PVC) frequently are used because they impart flame retardancy. Table 18 summarizes the non-lubricant applications and markets for chlorinated paraffins.

Table 18. Non-Lubricant Applications and Markets for Chlorinated Paraffins (Dover Chemical Corp., no date, a)

Applications

Aroclor (PCB's) Replacements	Resin Modifiers
Plasticizers - PVC Secondary Plasticizer	Flame Retardant - Chlorine Halogen Donor
Tackifiers	

Markets

Adhesives	Aqueous Base; Solvent Base; Hot Melt
Resin	Thermoset and Thermoplastic
Tapes	Pressure Sensitive
Coatings	Exterior Alkyl Modified, Chemical Resistant and Intumescent Fire-Retardant Paints
Rubber	Carpent Backing; Latex Compounding; Automotive Parts
Textile Finishing	Drapery, Upholstery and Wall Fabrics
Paper	Aluminum Foil to Paper Laminates
Vinyl	Plastisols and Custom Coaters
Laminates	
Ink	
Polymers	
Building Products	Insulation; Plywood
Electrical	Coatings for Electrical Cable

In order to understand the plasticizer and flame retardancy applications, one needs to be familiar with the mechanisms of plasticization and flame retardation. Plasticizers are materials incorporated in a plastic to increase its workability and its flexibility or distensibility (Darby and Sears, 1968). Secondary plasticizers are compounds that are not as completely compatible as primary plasticizers but can be substituted for primary plasticizers in order to lower the cost of the plasticized resin or to impart a desirable property to the formulation. PVC is the largest consumer of plasticizers (80% - Darby and Sears, 1968; Pattison and Hindersinn, 1971), and phthalate esters used with PVC amount to one-half of the total plasticizer production.

In the past, chlorinated paraffins were substituted for phthalate esters because they were less expensive (see Figure 4, p. 30, and Brighton, 1971; Bell et al., 1966; and Ball and Kolker, 1969). However, the volume cost estimates of Ball and Kolker (1969) were based upon a price for diisooctyl phthalate (DIOP) 1.67 times the price of chlorinated paraffins (52% Cℓ). The present price structure (chlorinated paraffins, 50% = $.265/lb; 60% = $.22/lb compared to DIOP = $.265/lb; Chemical Marketing Reporter, 1975) (Chlorowax 100 = $.27/lb, DIOP = $.26/lb; Anon., 1975d) would lead to much less, if any, financial savings. Nevertheless, sizable amounts of 40% -56% Cℓ (Brighton, 1971) chlorinated paraffins will continue to be used as secondary plasticizers with PVC, especially where flame retardancy and low temperature properties are important.

Although unplasticized PVC is self-extinquishing, the flame-retardant properties are reduced when it is plasticized with conventional compounds, such as phthalates and adipates. The phosphate ester plasticizers that are commonly used for flame retardancy have the disadvantage that the low-temperature strength of the PVC is considerably reduced (Bell et al., 1966, 1971; Brighton, 1971). Although chlorinated paraffin plasticized PVC has less low-temperature strength than DIOP-PVC, it is considerably better than the organophosphate plasticized PVC. Frequently antimony oxide, which is a synergistic flame retardant in the presence of a halogen source, is added with the chlorinated paraffins so that the required flame retardant properties can be reached without adding excessive amounts of chlorinated paraffins which might reduce the low temperature strength. Thus, for the above reasons and because chlorinated paraffins have high thermal stability, low discoloration

at elevated temperatures, low volatility (no more than conventional primary plasticizers) and are compatible (see Darby and Sears, 1968), the chemicals are extensively used as a secondary plasticizer with PVC. Major applications of the resulting PVC include electric cable, calendered film (for use in such applications as tarpaulins, mine ventilation, tubing, and decorative finishes in buildings), conveyor belting, and floor tile (Grant and Bilgor, 1966; Ball and Kolker, 1969; Bell et al., 1966). In most instances, the middle chlorination range (42-56% Cℓ) is used, although the materials with higher chlorine content are more compatible and, therefore, can be used in larger proportions (Brighton, 1971).

The use of chemicals to impart flame retardancy is one of the fastest growing markets for chlorinated paraffins. This is due to construction codes and government specifications which are being stiffened continuously. Building products using plastics have long been subject to stringent codes. "More recently, the Department of Transportation has imposed standards for automobiles and passenger vehicles; the Federal Aviation Authority, standards for internal components in aircraft; and the Department of Commerce, standards for carpets, mattresses, television, radio, and appliance housings" (Noble, 1974). Markets for textile flame retardants are probably the fastest growing due to the 1967 amendment of the 1953 Flammable Fabrics Act (Anon., 1975c, Drake, 1971). However, the flame retardant chemicals market for textiles is relatively small compared to that for carpeting (see Table 19).

Table 19. Flame Retardant Chemicals Market (Anon., 1975c)

Market	Total Lbs.	% of Market
Carpeting	250 million	70%
Textiles	10 million	3%
Plastics, coatings, and films	90 million	27%

As noted earlier, very little chlorinated paraffins are used for treating textiles with the exception of very heavy fabrics such as tents, tarpaulins, and awnings. However, because the textile market is relatively small, it has little effect on the chlorinated paraffins market.

Table 20 presents the annual estimated consumption of both additive and reactive intermediate flame retardants. These amounts are not completely compatible with the percentages in Table 16. For example, in

Table 20. U.S. Consumption of Miscellaneous Flame Retardants for Polymers (million lbs.) (Noble, 1974 - based upon data from Modern Plastics)

	1969	1972	1973
Additives			
Phosphate Esters			
Non-Halogenated	50.7	53.8	74.3
Halogenated	9.5	15.0	24.0
Chlorinated Paraffins	14.0	41.9	59.0
Antimony Oxide	16.0	17.6	19.0
Bromine Compounds	-	7.1	11.0
Boron Compounds	1.7	3.9	4.9
Other	5.7	10.1	18.2
	97.6	149.4	210.7
Reactive Intermediates			
Urethane	9.5	18.1	23.1
Polyester	13.0	11.4	15.0
Epoxy	1.7	5.3	8.4
Other	5.0	8.4	15.0
	29.2	43.2	61.5
TOTAL	126.8	192.6	272.2

1973, using the amounts in Table 20, flame retardancy applications would amount to 80% (59/73) of the total production. This is far greater than the percentage indicated in Table 16 (27%) for that year. However, the amounts for 1969 correspond fairly well (20% of 60 million lbs = 12 million lbs).

Flame retardants are chemicals used to reduce the burning ability of a particular material. There are four steps involved in burning: (1) preheating, where an external heating source warms the material, (2) decomposition, where the material degrades to combustible and volatile compounds, (3) ignition, where the compounds that are formed in the decomposition step are further heated and begin to burn, and (4) combustion and propagation, where the burning of the decomposition products results in enough heating of the material to provide a self-sustained flame (Pearce and Liepins, 1975; Pattison and Hindersinn, 1971). Inhibition of any of these steps results in a product with increased flame retardancy. The mechanism of halogen flame retardancy is not completely understood, but is frequently suggested to be due to dissipation by halogens of the highly reactive ·OH radicals which are needed for a high flame velocity. Similarly, no satisfactory theory is yet available to explain the synergistic effect between antimony compounds and halogenated flame retardants, but the formation of the volatile antimony trichloride or antimony oxychloride may be important in inhibiting free radical proliferation. However, other theories, such as the following mentioned by Pattison and Hindersinn (1971), may be equally as important as the mechanism for inhibition of radical chain reactions by halogens.

"Coating Theory - The fire-retardant additives intumesce or cause the formation of carbonaceous foam or char which acts as a thermal insulator in addition to preventing access of oxygen.

Gas Theory - Large volumes of incombustible gases are produced which dilute the oxygen supply. Examples are ammonia, nitrogen, sulfur dioxide, and halogen acid.

Thermal Theory - The fire retardant decomposes endothermally, e.g., by fusion or sublimation, or it undergoes an endothermic reaction with the flammable substrate which reduces the temperature below that at which the flame is self-sustaining.

Chemical Theory - It is suggested that species are formed which influence the course of the free-radical propagated combustion, reducing the ultimate flammability of the system." (Pattison and Hindersinn, 1971)

Flame retardancy can be provided by: (1) introducing additives prior to the polymer processing, (2) using additives as a finish or surface, (3) integrating a flame retardant comonomer before the polymerization, and (4) synthesizing inherently flame resistant structures (Pearce and Liepins, 1975). Chlorinated paraffins are used as additives which are usually added prior to the processing step. The ideal additive is inexpensive, colorless, easily blended, compatible, heat and light stable, efficient, permanent, and has no negative effects on the physical properties of the polymer (Pattison and Hindersinn, 1971). Because chlorinated paraffins exhibit high ratings in many of the above areas, they are used extensively as flame retardant additives.

The largest application of chlorinated paraffins for flame retardancy is probably in vinyl products (mostly PVC) which have been discussed previously. However, they also are used with other plastics such as polyesters, polyolefins (polyethylene and polypropylene), and polystyrene (Bell et al., 1966). Frequently, the 70% Cℓ grades of chlorinated paraffins are used with non-PVC plastics because of their higher compatibility. Chlorinated paraffins have reportedly been used with acrylics and modacrylics, polyurethane, and cumarone-indene resins (Hardie, 1964).

Chlorinated paraffins are also used in sizable quantities as flame retardant additives for rubbers such as chlorinated rubbers and neoprene. Large quantities of these materials are used for rug underlays and foam backings of carpets (see Table 19, p. 39) and for latex compounding and automobile parts. The chlorinated paraffins in many cases serve both as flame retardants and plasticizers.

Chemical resistant and fire retardant paints also provide a large market for chlorinated paraffins. In 1973, it was estimated that 4% of the total production of chlorinated paraffins was consumed in traffic paints (see Table 16, p. 33). The traffic paints, as well as many marine paints that use chlorinated paraffins, are usually rubber based (Wade, 1948; Ford, 1972; Jnojewyj and Rheineck, 1971). Chlorinated paraffins are effective as flame retardants in both solvent and water systems, and are recommended for both non-intumescent and intumescent paints (Diamond Shamrock Chem. Co., no date). Intumescent flame retardant paints contain additives which catalyze the decomposion of the paint film when subject to fire to produce a cellular (intumescent) char which insulates and protects the substrate. The higher chlorinated (70% Cℓ) resinous materials are used mostly to decrease the combustibility of the substrate, whereas the liquid chlorinated paraffins can serve also as plasticizers. Ford (1972) found that a binder composition of chlorinated rubber resin, chlorinated paraffin resin (Cereclor 70), and a liquid chlorinated paraffin (Cereclor 42) performed very well as a marine paint when field evaluated for four years in salt water. Such uses as traffic and marine paints and swimming pool enamels result from the improved flexibility and chemical and water resistance imparted by the chlorinated paraffins.

Chlorinated paraffins also find applications as tackifiers in aqueous and solvent base and hot melt adhesives. In fact, they have been suggested as replacements for Aroclor (PCB's) formulations in pressure sensitive adhesives (Dover Chemical Corp., no date b) (see Section II-B-4, p. 45).

2. Minor Uses

A number of minor uses of chlorinated paraffins have been patented or referred to in the available literature. These uses are tabulated in Table 21, along with the reference and the type of chlorinated paraffin when available.

Table 21. Minor Uses of Chlorinated Paraffins

Reference	Chlorinated Paraffin Used	Application
Scheer (1944)		Solvent for Dichloramine T in antiseptic nasal and throat sprays
		Chewing gum
		Emulsion type coatings applied to citrus fruits for preservation
		Mixture with terepenes as an insecticide
		Breaking petroleum emulsions
		Additive to castor oil to render soluble in mineral oil
		Catalyst in chlorination of methane
Roberts (1949)	<30% Cl	Lustering agents in dry-cleaning fluids for textiles
	<30% Cl	Substitute for olive oil in wood carding
	<30% Cl	Starting point for preparation of wax modifying agents
		Coating citrus fruit for preservation
		Ingredients in oils for waterproofing hides
		Component of foundry-core binder
		Flexible coating for carbon paper
		Component of moisture-resisting flexible films

Table 21. Minor Uses of Chlorinated Paraffins (continued)

Reference	Chlorinated Paraffin Used	Application
Hardie (1964)	70% Cl	Manufacture of dielectric fluids and insulating covering Adhesive anti-insect bands for fruit trees Marking inks Fumigating mixtures Surface active agents Soldering flux
From: Zitko and Arsenault (1974)		
Ban et al., (1972)		Antistatic agents for nylon
Komarek and Spahrkaes (1973)		Components of tanning composition
Prosser (1972)		Heat protecting coatings
Nakanishi and Kobayaski (1973)		Polysulfide compositions
Buell (1972)		Abrasive coated products
Morita and Sugiyama (1973)		Soot inhibitors for fuel oil
Horvath and Parsons (1972)		Coating for tableted calcium hypoclorite for use in treatment of sewage and swimming pool waters
Diery et al., (1972)	Chlorinated paraffin sulfonic acids	Emulsifiers of biocidal concentrates
Galloway (1958)		Improve effectiveness of pesticides by adding chlorinated paraffins to reduce volatilization
Bradbury and Fox (1958)	Cereclor 70	Additive to reduce phytotoxicity of γ-BHC-Hg seed dressings
Ali et al., (1971)		Wax emulsion with thiourea to prevent shrinkage and decay

3. Discontinued Uses

No references in the available literature mention termination of any major chlorinated paraffin application for health or environmental reasons. However, the use of chlorinated paraffins as a solvent for nasal and throat sprays, which was the first large application of chlorinated paraffins (Scheer, 1944), does not appear to be practiced today. The first large volume use of chlorinated paraffins was for making heavy textiles, especially canvas duck, flame resistant, waterproof, and mildewproof. Although a relatively small part of the total market, this application is still commercially important. Similarly, lubricant additive, plasticizer, and flame retardancy applications have not been discontinued.

4. Projected or Proposed Uses

Several references have mentioned that chlorinated paraffins may be a good substitute for some PCB applications. For example, Dover Chemical Corp. (no date,b) has compared the performance of chlorinated paraffins to the performance of PCB's in: (1) styrene-butadiene rubber based pressure sensitive adhesives, (2) thermoplastic type acrylic resin based pressure sensitive adhesives, and (3) crosslinked acrylic resin based pressure sensitive adhesives. In most instances, creep resistance was equal to or better than PCB formulations, and the tack and peel strength was maintained. Also, the chlorinated paraffin formulations exhibited excellent flame retardant character compared to PCB's, which is not too surprising since aliphatic halogen compounds are well-known to be more effective than aromatic halogen compounds (Pattison and Hindersinn, 1971). In some formulations, the heat stability of the chlorinated paraffin products was slightly less than with PCB's.

Ford (1972) investigated the performance of chlorinated rubber paints under marine conditions using both PCB or chlorinated paraffin binder formulations. The paint containing PCB's gave the best results, but the chlorinated paraffin blend gave good results and was considered to be a high performance binder.

Based upon the properties of chlorinated paraffins, it seems likely that the following applications in which PCB's were used in 1970 (Nisbet and Sarofim, 1972) may be using chlorinated paraffins: plasticizer applications in synthetic resins, adhesives, and rubbers; wax extenders; dedusting agents; inks; lubricants; cutting oils; and carbonless reproducing paper. In contrast, applications which are dependent upon the high heat stability of PCB's (e.g., heat transfer, capacitors, and transformers) are not candidates for chlorinated paraffin replacement because of the comparitively low thermal stability of the chlorinated paraffins.

Chiba and Adachi (1970) have patented the use of chlorinated paraffins as a paper-sizing agent (render the paper more resistant to penetration by liquids, particularly water). It is possible that the chlorinated paraffins containing 70% chlorine could completely replace the normally used resin (Vizante et al., 1972; Zitko and Arsenault, 1974).

5. Possible Alternatives to Uses

None of the applications of chlorinated paraffins could be termed as a matter of convenience; the applications are for the most part essential for the commercial function of the final product. At one time, chlorinated paraffins were added as a secondary plasticizer to PVC mostly for economic reasons; chlorinated paraffins were cheaper than the primary plasticizer.

However, the flame retardant properties imparted by the chlorinated paraffins to such products as carpet backing and vinyl tiles are essential now due to modified building codes and government regulations. Organophosphorus plasticizers could be used instead, but they appear to be more expensive (Brighton, 1971) and they reduce the low temperature strength of the plasticized resin compared to chlorinated paraffins-plasticized PVC (Brighton, 1971; Bell et al., 1971). Other options include using other flame retardant plasticizers or inherently flame resistant monomers (see Table 22), but again cost is an important factor.

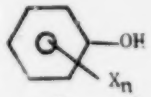
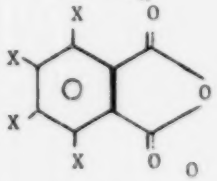
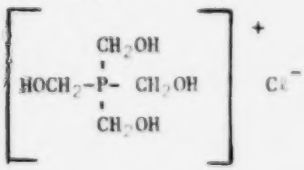
A number of alternatives to lubricant and cutting oil additive applications of chlorinated paraffins are possible. This is the oldest and still one of the largest applications for chlorinated paraffins. These chlorinated compounds can provide both boundary lubrication and extreme pressure activity. The chlorinated paraffins are part of a group of antiwear agents which are required to minimize function and wear. Under boundary film conditions, there are six main groups of chemicals that could be used instead of the chlorinated paraffins: (1) compounds containing oxygen (fatty acids, esters, ketones); (2) compounds containing sulfur or combinations of oxygen and sulfur; (3) organic sulfur compounds (sulfurized fats, sulfurized olefins); (4) compounds containing both chlorine and sulfur; (5) organic phosphorus compounds (tricresyl phosphate, thiophosphates, phosphites); and (6) organic lead compounds (Lee and Booser, 1967). Applicability will depend upon the film-forming ability of the chemical group with specific metals or other materials. Under extreme rubbing conditions where extreme pressure additives are required, active sulfur, phosphorus and lead compounds or other halogen compounds might be substituted for the chlorine compounds (Lee and Booser, 1967; Matthijsen and Van Den Brekel, 1967).

Other chlorinated organic compounds, such as trichloroethylene, tetrachloroethane, carbon tetrachloride, and o-dichlorobenzene, might be considered as alternatives, but they usually have severe medical and health problems (Matthijsen and Van Den Brekel, 1967).

Flame retardancy can be imparted to commercial products in a number of ways besides using flame retardant additives; for example, (1) use a flame retardant finish or surface, (2) integrate a flame retardant monomer into the polymer, or (3) synthesize inherently flame resistant structures (Pearce and Liepins, 1975). The inherently fire retardant polymers, such as polybenzimidazoles and aromatic polyamides, are extremely expensive and, therefore, are not likely to replace sizable portions of the chlorinated paraffin flame retardant market. However, they are being used in markets, such as aircraft applications, where the smoke and fumes generally produced by halogenated flame retardants cannot be tolerated. In fact, Pattison and Hindersinn (1971) have suggested that the smoke and corrosive fumes generated when halogenated materials are exposed to fire may limit their future growth.

Flame retardancy is obtained when sufficient quantities of halogens, phosphorus, nitrogen, or boron are present (Noble, 1974). Thus, any compounds that contain these elements might be substitutes for chlorinated paraffins. In addition, compounds that have synergistic flame retardant effects, such as antimony oxide, may be considered. Factors which have to be considered in determining replacements for chlorinated paraffins are expense, color of the additive, ease of formulation, compatibility, heat and light stability, flame retardant efficiency, permanency, and effect on the physical effects of the polymer (Pattison and Hindersinn, 1971). Environmental compatibility is also an important parameter that should be considered. Possible replacements for chlorinated paraffins are listed in Table 22.

Table 22. Possible Replacements for Flame Retardant Applications of Chlorinated Paraffins (Pattison and Hindersinn, 1971; Pearce and Liepins, 1975)

Additives	Example
Non-reactive, Organic	
Phosphate esters	$[CH_3(CH_2)_7O]_3P{=}O$
Halogenated phosphate esters	$(BrCH_2CHBrCH_2O)_3P{=}O$
Halogenated phosphonate esters	$(CH_3CH_2O)_2\overset{O}{\overset{\|}{P}}\text{-}CH_2CH_2Br$
Halogenated hydrocarbons	Hexabromocyclododecane Pentabromotoluene
Polyvinyl chloride (physically blended)	
Polyvinylidene chloride (physically blended)	
Non-reactive, Inorganic	
Antimony oxide	Sb_4O_6
Aluminum oxide trihydrade	$Al_2O_3\text{-}3H_2O$
Zinc borate	$Zn_2B_6O_{11}$
Ammonium orthophosphate	$(NH_4)_3PO_4$
Ammonium sulfamate	$NH_4SO_3NH_2$
Reactive	
Bromine and/or phosphorus containing polyols	CH_2OOCR CH_2OOCR CH_2OOCR R = OH $CH_3(CH_2)_5CH\ CH\ CH\text{-}(CH_2)\text{-}$ Br Br
Halogenated phenols	
Tetrahalophthalic anhydride	
Phosphonate esters	$H(OCH_2CH_2)_nO\overset{O}{\overset{\|}{P}}\ CH_2OH$
Dibromopentyl alcohol	$(BrCH_2)_2C(CH_2OH)_2$
Tetrakis(hydroxymethyl)phosphonium chloride (THPC)	
Vinyl chloride or bromide	$CH_2 = CHCl, Br$
Vinylidene chloride	$CH_2 = CCl_2$

C. Environmental Contamination

1. General

Unfortunately very little substantive information is available which would allow an estimation of the amount of chlorinated paraffins being released to the environment. No monitoring has been reported, mostly because adequate analytical techniques have not been developed. Therefore, almost all of the discussion in this section is based upon speculation. Throughout this section, comparison will be made between chlorinated paraffins and the well-known environmental contaminants, polychlorinated biphenyls (PCB's), because of the similarities in terms of physical properties and some applications. This comparison was facilitated by the work of Nisbet and Sarofim (1972) and Zitko and Arsenault (1974).

Zitko and Arsenault (1974) have compared some physical and chemical properties of the two chemical groups which are relevant to considerations of environment contamination. Their information as well as some other available data are summarized in Table 23.

2. From Production

Chlorinated paraffins are manufactured by eight chemical producers in plants located in ten different cities across the country (see Table 13, p. 24). Production in 1973 amounted to 74 million pounds (see Table 12, p. 22), which is about equal to the sales of PCB's for the year 1970 (the largest amount sold in one year).

Chlorinated paraffins are made by liquid phase chlorination of either: (1) the liquid paraffin, which is frequently heated to decrease the viscosity and increase the rate of chlorination, or (2) the paraffin dissolved in a solvent such as carbon tetrachloride. No contact is made with water,

Table 23. Comparison of PCB and Chlorinated Paraffin Physiochemical Properties Relevant to Environmental Contamination Considerations (Nisbet and Sarofim, 1972; Zitko and Arsenault, 1974; Hardie, 1964)

Properties	Compounds		Remarks
	Chlorinated Paraffins	PCB's	
Vapor Pressure (mm Hg)	2×10^{-5} ($C_{23}H_{48}$ - 42-54%Cl)	10^{-4} (Aroclor 1242) to 2×10^{-7} (Aroclor 1260)	The high molecular weight chlorinated paraffins (C_{20}- C_{30}) are probably less volatile than PCB's. The C_9-C_{15}, more volatile.
Water solubility		25-200 ppb	No information on chlorinated paraffins. Based upon solubility of the parent hydrocarbon, probably equal to or less soluble than PCB's
Thermal stability	Extensive decomposition at 300-400°	Stable up to 800°C	PCB's volatilize before decomposition. Chlorinated paraffins decompose before volatilization.

and, therefore, loss in water effluents should be negligible. After chlorination, the product is stripped of solvent (used only with higher chlorinated products), and air or other gases are blown through the product to remove residue chlorine gas and hydrogen chloride. This stripping might result in loss of some of the lower chlorinated isomers, but since the more volatile chlorine gas and hydrogen chloride are recovered, the loss is suspected to be very low.

Occasionally the final product will not meet the quality control standards and will have to be disposed of or reformulated, if possible. The amount of material that falls into this category is unknown but is likely not to be very substantial for economic reasons. If it is recovered, no loss to the environment occurs. Disposal will be discussed in Section II-C-5, p. 55.

3. From Transport and Storage

Small quantities of the liquid chlorinated paraffins are transported and stored in 55 gallon drums. Bulk quantities are transported in insulated and heated tank cars or trucks and stored in insulated and heated tanks. Disposal of non-returnable drums might result in some environmental release. Also, if storage or transportation tanks are cleaned out for other chemical use, environmental release might occur. Storage tanks are vented to the atmosphere (Hardie, 1964), but the low volatility would suggest negligible losses. Spills may occur, but the high viscosity and water insolubility of the material makes cleanup using an absorbent material fairly easy. The cleaned up material would probably be deposited in a landfill.

4. From Use

The uses of chlorinated paraffins probably provide the major source of environmental contamination. Many of the chlorinated paraffin applications are identical to the ones suspected as being the major sources of PCB contamination. Table 24 compares the applications of PCB's and chlorinated paraffins.

Table 24. Applications of PCB's and Chlorinated Paraffins (percentage of total)

Applications	PCB's (Nisbet and Sarofim, 1972)	Chlorinated Paraffins (this report)
Electrical and heat transfer (closed systems)	60%	0%
Plasticizer	25%	24%
Hydraulic fluids and lubricants	10%	45%
Miscellaneous (including surface coatings, adhesives, printing inks, and flame retardants)	5%	31%

Using the same assumptions as Nisbet and Sarofim (1972), it is possible to calculate some approximate losses from plasticizer and oil additive applications. Nisbet and Sarofim (1972) concluded that lubricants are rarely reused and, therefore, the amount scrapped each year is approximately equal to the amount sold for that application (45% x 76 x 10^6 lbs. = 34 x 10^6 lbs. for chlorinated paraffins in 1973). A sizable amount of the discarded oil will be deposited in dumps or landfills. Also, a significant quantity of any chlorinated paraffin used in automotive and industrial lubricant oils will probably reach water resources via storm drains (Anon., 1972).

Behavior of chlorinated paraffins compared to PCB's in plastics can be estimated from some plasticizer performance data provided by Darby and Sears (1968) (Table 25).

Table 25. Plasticizer Performance of PCB's and Chlorinated Paraffins in PVC (Darby and Sears, 1968)

Plasticizer	Volatility plasticizer loss, %, 24 hr., 87°C	Water extraction % loss, 24 hr., 50°C	Kerosene extraction % loss, 24 hr., 23°C
Chlorinated (54% Cℓ) biphenyl			
40% PCB	9.1	0.08	2.6
20% DIOP & 20% PCB	18.4	0.04	12.2
Chlorinated (52% Cℓ) paraffin 40%	6.1	0.01	1.7

Nisbet and Sarofim (1972) estimated the rate of evaporation of PCB's from plastics was approximately 10 to 20% of sales. Since chlorinated paraffins are somewhat less volatile (at least with the formulations given by Darby and Sears, 1972), the chlorinated paraffin loss is probably 10% of sales ($.10 \times .24 \times 76 \times 10^6$ lbs. = 1.7×10^6 lbs.). The remaining plasticizer ($.90 \times .24 \times 76 \times 10^6$ lbs. = 16.7×10^6 lbs.) is probably discarded in dumps because of the short useful life of most plastics.

Sizable releases to the environment from chlorinated paraffin flame retardant applications are also likely, but more difficult to quantitate. Chlorinated paraffin flame retardants in plastics are probably susceptible to the same losses as secondary plasticizer applications. Building materials using chlorinated paraffin flame retardants probably eventually end up in dumps, but have a much longer useful life than plastics.

Loss from leaching of chlorinated paraffins from external, marine, and traffic paints probably also contribute significantly to environmental contamination.

5. From Disposal

Although the amounts of chlorinated paraffins that are disposed of every year are unknown, it is likely that disposal methods consist of either incineration or landfilling. Incineration should result in complete destruction of chlorinated paraffin materials because of their relatively low thermal stability. On the other hand, Zitko and Arsenault (1974) have suggested that the possibility of thermal formation of low molecular weight chlorinated hydrocarbons from chlorinated paraffins should be investigated, especially in view of the carcinogenicity of some of the low molecular weight compounds.

There is a high probability that large quantities of chlorinated paraffins will reach landfills as a result of disposal of such products as plastics, waste oils, and products that use flame retardants. However, because of the low water solubility of chlorinated paraffins relative to PCB's (see Table 23, p. 51, and 25, p. 54), it is likely that much less leaching of chlorinated paraffins from landfills and dumps will occur.

6. Potential Inadvertent Production of Chlorinated Paraffins in Other Industrial Processes

Chlorinated paraffins might be produced as a by-product from chlorination of other hydrocarbon feed stocks, if significant amounts of paraffin are present as contaminants in the hydrocarbon starting material. With hexachlorobenzenes and hexachlorobutadiene, inadvertent production appears to be a major environmental contamination source (Mumma and Lawless, 1975). Since paraffins as well as many other hydrocarbons are derived from

petroleum feed stocks, the possibility of inadvertent chlorinated paraffin contamination from chlorination of hydrocarbons seems feasible at first glance.

A large portion (59%) of the chlorine that is consumed in this country (9.868 billion lbs./year) is used in chlorinating hydrocarbons (Mumma and Lawless, 1975). Table 26 lists the major compounds which are chlorinated and, when available, the quantities of the final product that are manufactured. In most of these hydrocarbons the possibility of paraffin contamination seems very remote. Some of the organic compounds are gases and most of them are distilled or fractionated in some way before chlorination. Those compounds should have no high molecular weight paraffins because of the high boiling points of the paraffins. However, some less volatile compounds, such as α-pinene, naphthalene, and biphenyl, might have small amounts of paraffins.

Another possible by-product source of chlorinated paraffins is from the incomplete polymerization of chlorinated ethylene monomers (e.g., vinyl chloride, 1,2-dichloroethylene). If the polymerization process is incomplete, lower-molecular weight products will be formed that closely resemble the chlorinated paraffins. The quantity of chlorinated paraffins produced in this way is unknown, but could be quite large considering the volume of polyvinyl chloride produced every year.

7. Potential Inadvertent Production in the Environment

Although there are approximately 150 naturally occurring chlorine compounds that have been identified so far (Siuda and DeBernardis, 1973), it does not appear likely that the chlorinated paraffins, with their

Table 26. Organic Compounds That Are Produced By Direct Chlorination (from Mumma and Lawless, 1975)

Starting Material	Product	Product (X 10^6/year)
Acrylic		
Methane or Methanol	Methyl chloride	222/1970
	Methylene chloride	260/1970
	Chloroform	118/1970
	Carbon tetrachloride	496/1970
Ethane or Propane	Perchloroethylene	
	Carbon tetrachloride	
Ethane	Methyl chloroform	
Ethylene	Ethylene dichloride	4420/
Ethanol or Acetaldehyde	Chloral	31/1969
Acetylene	Perchloroethylene	
	Trichloroethylene	
Acetylene	Chloroprene	
	Vinyl chloride	
1,3-Butadiene	1,4-Dichlorobutene	154/1970
	Chloroprene	114/1970
Acetic acid	Monochloroacetic acid	34/
	Trichloroacetic acid	4/
Cyclic		
Benzene	Monochlorobenzene	243/1970
	o-Dichlorobenzene	50/1970
	p-Dichlorobenzene	60/1970
	Trichlorobenzenes	4.5/1970
	Benzene hexachloride (use U.V. light during synthesis)	1/
Toluene	Benzyl chloride	43/
	Benzal chloride	2/
	Benzotrichloride	9/
	Chlorotoluenes	38/1971
α-Pinene	Toxaphene	25
Cyclopentadiene	Hexachlorocydopentidiene	25/1971
Nitrobenzene	Monochloronitrobenzenes	444/1970
	Pentachloronitrobenzene	1.5/1970
Naphthalene	Chlorinated naphthalenes	2.5
Biphenyls	Polychlorinated biphenyls	20

high chlorine content, will be produced in nature. However, there are sizable amounts of paraffinic hydrocarbons in the environment that are formed from natural as well as man made processes (see Table 27). Since chlorine is used in both waste water and drinking water treatment, it is possible that chlorinated paraffins could result. Because of the dilute conditions that prevail, only very low numbers of chlorine atoms per molecule (mono- or dichloro compounds) seem at all likely.

Table 27. Paraffinic Hydrocarbons Identified in Industrial Effluents (Abrams et al., 1975)

Paraffin	Formula
n-dodecane	$C_{12}H_{26}$
n-docosane	$C_{22}H_{46}$
eicosane	$C_{20}H_{42}$
hexadecane	$C_{16}H_{24}$
nomane	C_9H_{20}
octadecane	$C_{18}H_{38}$
octane	C_8H_{18}
pentadecane	$C_{15}H_{32}$
tetradecane	$C_{14}H_{30}$
n-tridecane	$C_{13}H_{28}$
n-undecane	$C_{11}H_{24}$

D. Current Handling Practices and Control Technology

1. Special Handling in Use

No special safety precautions are necessary for handling chlorinated paraffins. Most of the commercial formulations have no effects on the skin, on repeated or prolonged contact (Hardie, 1964), but protective gloves are recommended (Diamond Shamrock Chem. Co., 1972). It is also suggested that safety glasses and body length clothing be worn and that respiratory protection equipment be used when working in aerosol mists of liquid chlorinated paraffins (Diamond Shamrock Chem. Co., 1972). No threshold limit values for allowed exposure have been established. When working with the higher chlorine-content paraffins (70%), it is recommended that proper ventilation be provided because of residual amounts of the highly toxic carbon tetrachloride, which is frequently used as a solvent in their manufacture (Hardie, 1964).

Temperatures exceeding 400°F and strong bases as well as exposure to hot or finely divided metals of the third and fourth periods of the periodic chart should be avoided. Storage temperatures should not exceed 66°C for more than several hours in vented containers or 40°C in closed vessels (Diamond Shamrock Chem. Co., 1972).

2. Methods for Transport and Storage

The liquid chlorinated paraffins are transported in drums (usually 55 gallon) and insulated tank cars or tank trucks. Bulk shipments may vary from 4,000 - 10,000 gallons. The solid chlorinated paraffins are transported in the form of solid broken lumps in lined sacks of paper or other material.

Stainless steel or lead-, glass-, enamel-, or lacquer-lined mild steel are frequently used as container material for the liquid chlorinated paraffins, although all-welded mild steel containers can be used if the storage temperature does not exceed 30°C (Hardie, 1964). When color deterioration is unacceptable (caused by traces of iron), the drums may be internally lacquered with a phenol-formaldehyde resin (Hardie, 1964). The sacks for the solid chlorinated paraffins are lined with polyethylene, at least in the United Kingdom (Hardie, 1964).

Liquid chlorinated paraffins can be loaded or unloaded by a pump, by air pressure, or in some cases, by gravity (Diamond Shamrock Chem. Co., 1974). When compressed air is used, it should be entirely free of suspended matter, such as iron rust particles, which may catalyze decomposition and decoloration. Since many of the products are very viscous, the tank cars and trucks as well as storage tanks are frequently insulated and contain heating coils to facilitate transfer. The Diamond Shamrock Chemical Co. (1974) recommends that pipes be lined with polyvinylidene dichloride.

As noted earlier, storage temperatures should not exceed 66°C in vented containers or 40°C in closed vessels.

3. Disposal Methods

No special disposal procedures are recommended. Diamond Shamrock Chemical Co. (1972) suggests that federal, state and local regulations regarding health and pollution be followed.

Because chlorinated paraffins decompose at relatively low temperatures (300-400°C) compared to PCB's (>800°C), they can be disposed of with conventional incinerators without the need for special precautions

(e.g., afterburners). It is suspected that the chlorinated paraffins would decompose in an incinerator before significant amounts are volatilized (Zitko and Arsenault, 1974). Some control of the hydrogen chloride generated would probably be required.

4. Accident Procedures

If liquid chlorinated paraffins are spilled or released, they should be covered with an oil-absorbent type material, swept up and disposed of in an acceptable manner. All of the chlorinated paraffin formulations are considered to be non-flammable, but the liquid products are free flowing, especially when they are hot, and therefore, should be treated as an oil in a fire area. In a fire area, noxious and corrosive gases, such as phosgene and hydrogen chloride may be generated, and therefore, firefighters should avoid confined areas containing these materials. Furthermore, these gases may cause rupture of non-vented containing vessels (Diamond Shamrock Chem. Co., 1972).

The following procedures are recommended for first aid in case of human contact with chlorinated paraffins (Diamond Shamrock Chem. Co., 1972):

Skin contact - wash with soapy water

Eye contact - flush with warm water

Ingestion - consult a physician

5. Current Controls

No controls on chlorinated paraffins handling or use have been located in the available literature. The Interstate Commerce Commission does not require any special packaging.

6. Control Technology Under Development

None identified in the available literature.

E. Monitoring and Analysis

1. Analytical Methods

Analysis of trace amounts of technical chlorinated paraffins is difficult due to the complexity of the formulations. Zitko and Arsenault (1974) have reviewed possible cleanup and analysis techniques that could be used with chlorinated paraffin. The less applicable techniques that were reviewed will be briefly discussed here, followed by detailed consideration of the more promising methods.

The fact that chlorinated paraffins are part of the chlorinated hydrocarbon family suggests that analytical techniques used with organochlorine pesticides and PCB's might be applicable for trace detection of chlorinated paraffins. Determination of chlorine has been shown to be an effective means of quantitation for the chlorinated paraffins, but the more sensitive or specific techniques used with pesticides, such as gas chromatography with electron capture detection (GC-EC) or gas chromatography combined with mass spectrometry (GC-MS), do not appear to be feasible.

Zitko and Arsenault (1974) stated that the mass spectra of chlorinated paraffins are of little diagnostic value, except for a few peaks at low masses. This statement was based upon review of a paper by Valovoi and Polyakova (1970) as well as a private communication with Hutzinger and Safe of the National Research Council of Canada. Friedman and Lombardo (1975) have considered the possibility of using the GC-EC technique for detection of chlorinated paraffins. Unfortunately, electron capture is relatively

insensitive to aliphatic compounds such as chlorinated paraffins (e.g., 500 μg of Chlorowax 500C was required for ½ full scale deflection - Lombardo et al., 1975). As a result, the chlorinated paraffin gas chromatographic peak pattern is obscured by the commonly found chlorinated aromatic compounds (e.g., DDT and PCB's), which cause large responses with electron capture detectors. The UV irradiation cleanup step devised by Friedman and Lombardo (1975) helped somewhat (e.g., the interfering DDE peaks were totally removed), but the chlorinated paraffins still only appeared as "a series of poorly defined bumps on a huge 'solvent' tail" (Lombardo et al., 1975).

Less sensitive techniques such as infrared spectrometry have been used to analyze chlorinated paraffins. Roesner and Berthold (1965) used the 615 cm^{-1} C-Cℓ stretching frequency for quantitation. Cachia et al. (1958) also used infrared spectroscopy to detect chlorinated paraffins in mixtures of plasticizers. The chlorinated hydrocarbon plasticizers (e.g., Cereclor I or Arochlor 1242) were separated from the other plasticizers by silica gel column chromatography using carbon tetrachloride solvent.

Zitko and Arsenault (1974) have suggested that high pressure liquid chromatography may have great potential for isolation and quantitation of chlorinated paraffins if a microcoulometric or electrolytic conductivity detector were used. This especially applies to the formulations that have high chlorine content or long carbon chains and thus may decompose at temperatures required for elution with conventional gas chromatography. So far, use of the liquid chromatographic technique has not been reported.

Determination of chlorine, especially by microcoulometry, is, so far, the most frequently used method for quantitating trace amounts of chlorinated paraffins. Zitko and Arsenault (1974) suggest that the available methods that could be used with chlorinated paraffins include determination of chlorine, titrimetrically with silver nitrate, by halogen-selective electrodes, or microcoulometrically. The chlorine may be in the form of hydrochloric acid, or chloride liberated from the sample either by combustion or by reduction with metallic sodium (Zitko and Arsenault, 1974). Table 28 presents some of the chlorine detection techniques that were reviewed and evaluated by Zitko and Arsenault (1974). However, only the thin layer silver nitrate - UV detection technique noted in Table 28 has actually been used with chlorinated paraffins.

Zitko and Arsenault (1974) examined the thin layer chromatographic (TLC) properties of Cereclor 42 and Chlorez 700. The study concentrated on silica layers because they provided much less diffuse spots than alumina. Conventional silver nitrate, 2-phenoxyethanol and acetone spray followed by UV light development resulted in a detection limit of 130 and 2 µg for Cereclor 42 and Chlorez 700, respectively. By slight modification (spraying with 1 N $AgNO_3$, 0.1% fluorescein in 50% aqueous ethanol and heating to 100°C for 10 min.), the authors increased the limit of detection to 8-10 µg for Cereclor 42. However, the detectable concentration of chlorinated paraffins in lipids is only 10 and 1% for Cereclor 42 and Chlorez 700, respectively. Thus, in order to use the TLC procedure, the lipids would have to be separated from the chlorinated paraffins. Thin layer chromatography with silver nitrate detection was not considered any further by Zitko and Arsenault (1974) or by any other investigator.

Table 28. Analytical Methods of Chlorine Detection (Zitko and Arsenault, 1974)

Reference	Chlorine Liberation Technique	Chlorine Detection	Sensitivity	Remarks
Koblitsky et al. (1962)	Sodium reduction	Microcoulometry	5 µg/g	Never widely used because of lack of specificity compared to gas chromatographic methods
Krijgsman et al. (1970)	Combustion	Titration $AgNO_3$ Ag-selective ion electron	0.1 - 10 µeq	Has problems in recovery of hydrogen chloride from combustion
Hassan (1973)	Combustion	Chloride - selective electrode		
Volodina et al. (1973)	Glow discharge in ammonia atmosphere	Chloride determined argentometrically		
Chumachenko and Alekseeva (1971)	Pyrolysis in presence of saturated hydrocarbons	HCℓ separated from dicyan and H_2S by chromatography - $HgNO_3$ solution conductometrically		
Koppe and Rautenberg (1970a & b)	-	$AgNO_3$ under UV light on thin layers of silica		Well known reaction for detection of chlorinated hydrocarbon pesticides

Zitko (1973) has used a commercially available combustion furnace and microcoulometer (Dohrman microcoulometric system MCTS-20) with high-molecular-weight chlorinated paraffins (C_{20} - C_{24}). The combination of gas liquid chromatography with microcoulometric detection was not used because of the low volatility of the formulations. Cereclor 42 (I.C.I., 42% chlorine) and Chlorez 700 (Dover Chemical, 70% chlorine) were the two chlorinated paraffins studied. Recovery of chloride from the chlorinated paraffins was only 40-60% when hexane was used as the solvent for injecti n (probably due to the rapid evaporation of hexane in the needle). Much higher yields were obtained (80-90%) when solutions of 20 w/v% diethylhexyl phthalate (DEHP) or Nujol in hexane are injected. Sensitivity of this system is 2 ng of chloride (Zitko and Arsenault, 1974).

Unfortunately, determination of chlorine by direct microcoulometry is not a specific method for quantitation of chlorinated paraffins. Sulfur and nitrogen compounds may interfere as well as other organochlorine compounds, both man-made and natural. For example, Siuda and DeBernardis (1973) suggest that the number of "naturally occurring" halogenated compounds total more than 200. Lombardo and coworkers (Friedman and Lombardo, 1975; Lombardo et al., 1975) have made the microcoulometric detector somewhat more specific by combining it with a gas-liquid chromatographic column. However, this technique could only be used with the shorter (C_{12} - C_{17}) chlorinated paraffins, because the longer chained materials would decompose on the column. The chlorinated paraffins used by Friedman and Lombardo (1975)

were Chlorowax 500 C (C_{12}, chlorine=59%, Diamond Shamrock), Unichlor 70LV (C_{12-14}, chlorine=69%, Neville Chem. Co.), Cereclor S-45 and Cereclor S-52 (C_{14-17}, chlorine=45% and 52%, respectively, ICI America Inc). Using this combined technique, Friedman and Lombardo (1975) were able to readily quantitate chlorinated paraffins at the ppm level. Lombardo et al. (1975) were able to get ½ full scale deflection with 300 µg of Chlorowax 500 C (electron capture required 500 µg).

Even combined gas chromatography-microcoulometry is susceptible to interferences from normally encountered environmental contaminants. Furthermore, since it can only be used with the more volatile chlorinated paraffin formulations, it has limited applicability. Therefore, several approaches have been suggested for either cleaning up the sample before quantitation or chemically modifying the chlorinated paraffin to allow more specificity during quantitation.

Zitko (1974b) examined the possibility of using a reductive dechlorination confirmatory test for chlorinated paraffins. Dechlorination could allow identification by the gas chromatographic peak pattern of the parent paraffin mixture. Zitko (1974b) used sodium bis(2-methoxyethoxy)-aluminum hydride as the dechlorinating agent. Yields of the parent hydrocarbon varied from approximately 15-30% for the formulations containing 40% chlorine, to 9% for the 50% chlorine, to no detectable paraffin for the 70% chlorine formulation (see Table 11, p. 20). With the hydride used, it has been shown that vicinally disubstituted alkanes give the respective alkenes,

and therefore, it is understandable that reduction of the formulation containing 70% chlorine (almost one chlorine on every carbon atom) resulted in no paraffins. The unsaturated products from reduction of the 70% chlorine product also contain hydroxyl function and fluorescence with an excitation maximum at 320-340 nm and an emission maximum at 450 nm.

The reduction process can be carried out on relatively clean samples of chlorinated paraffins as well as in the presence of lipids (excess reducing agent is used). Alumina column chromatography was used for removing the lipids after reduction.

This dechlorination procedure followed by gas chromatographic-flame ionization detection (GC-FI) of the paraffinic hydrocarbons may be used as a confirmatory test for chlorinated paraffins containing up to 50% chlorine. However, reductive dechlorination of chlorinated paraffins containing 70% chlorine does not yield paraffin hydrocarbons, but instead results in unsaturated compounds that may also be used for confirmatory purposes, especially if their fluorescence spectra are recorded. As with many confirmatory tests, the dechlorination technique is much less sensitive than microcoulometric detection. "The limit of detection for Cereclor 42 is 25 mg/g lipid. At the same concentration of Chlorez 700, the bluish fluorescence was clearly visible on TLC plates" (Zitko, 1974b). The reductive dechlorination technique using sodium bis(2-methoxyethoxy)aluminum hydride and GC-FI has also been used by Panzel and Ballschmiter (1974) to identify and determine trace amounts of chlorinated paraffins (see Figure 1, p. 2).

Most other approaches to making the detection of chlorinated paraffins more specific have been directed toward removal of interfering compounds before quantitation by microcoulometry. Friedman and Lombardo (1975) developed a photochemical technique for eliminating chlorinated aromatic interferences. By irradiating the sample contained in petroleum ether for 90 minutes with high energy ultraviolet light, they were able to eliminate 100% of the peaks attributed to o,p'-DDE, p,p'-TDE, perthane, carbophenothion, p,p'-DDT, methoxychlor, Halowax 1099 (chlorinated naphthalene), and Arochlor 1254 (PCB's). However, cycloaliphatic materials such as toxaphene, chlordane, strobane, and mirex were not totally destroyed. Quantitation was provided by gas chromatography with microcoulometric detection. Recovery studies of ocean perch fillets fortified with 1 and 5 ppm Chlorowax 500C indicated >90% recovery when the method of Porter et al. (1970) was used followed by irradiation. The procedure of Porter et al. (1970) consists of petroleum ether extraction of the fish or animal tissue, petroleum ether-acetonitrile partitioning (to remove lipids), followed by Florisil column chromatography. The 6% ethyl ether-petroleum ether eluate is the one irradiated in the Friedman and Lombardo (1975) technique. This same procedure was used by Lombardo et al. (1975) to detect the amount of chlorinated paraffin in rainbow trout fed a diet of 10 ppm Chlorowax 500C (C_{12}). Recoveries from fortified samples were greater than 92% and the sensitivity was at least 0.5 ppm.

Zitko (1973) devised a chromatographic procedure which could clean up biological extracts containing chlorinated paraffins and also separate PCB's from the chlorinated paraffins. Fortified samples of herring gull yolk, common seal blubber, and fish food were extracted with hexane and then the extract was chromatographed on alumina to remove the lipids. Recovery of the chlorinated paraffins is quantitative. The elution pattern from the alumina column was affected by the quantity of lipids present, probably due to deactivation of the alumina by the lipids (Zitko, 1973). Using silica chromatography on the alumina column eluate, PCB's and p,p'-DDE (hexane eluate) were separated from other chlorinated hydrocarbon pesticides and the chlorinated paraffins being studied (10% ether in hexane eluate). Alumina chromatography has a tendency to reduce the "apparent chlorine" background (direct microcoulometric detection) in the biological samples as noted in Table 29. Table 29 also illustrates that sizable quantities of "apparent chlorine" pass through the alumina column but cannot be attributed to PCB or DDT compounds, and this accentuates the non-specificity of direct microcoulometry.

Table 29. Effect of Alumina Chromatography on the Apparent Chlorine Content in Various Biological Samples (data from Zitko, 1973)

Sample	µg/g wet wt hexane extract	µg/g in hexane fraction from alumina column	% PCB and DDT in hexane fraction from alumina column
Herring gull yolk	214	17.6	57%
Fish food	3.00	1.11	20%
Seal blubber	94	94	71%

Zitko and Arsenault (1974) have examined the solvent partitioning of chlorinated paraffins as well as the extraction recoveries of chlorinated paraffin fortified sediment samples. Solvent partitioning is a frequently used cleanup procedure (e.g., the Porter et al., 1970, procedure used by Lombardo et al., 1975) and can be used as a confirmatory technique. Lombardo et al. (1975) have demonstrated that the shorter chain (C_9 - C_{17}) could be partitioned away from lipids using petroleum ether and acetonitrile. Zitko and Arsenault (1974) examined the recovery of the longer chained (C_{20} - C_{25}) chlorinated paraffins from hexane solution into acetonitrile (MeCN), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO). The results of their partitioning study are presented in Table 30.

Table 30. Recovery of Chlorinated Paraffins from Hexane (Zitko and Arsenault, 1974)

	Cumulative Recovery, %					
	Cereclor 42			Chlorez 700		
Extraction No.	MeCN	DMF	DMSO	MeCN	DMF	DMSO
1	46.9	70.7	33.3	31.6	69.9	88.0
2	66.2	86.3	43.3	59.3	93.1	93.3
3	85.3		59.1	71.4		95.1

The results demonstrate that hexane-DMF could be used as a cleanup procedure to remove lipids. However, Zitko and Arsenault (1974) concluded that "not enough data are yet available to use solvent partitioning of chlorinated paraffins as a diagnostic tool."

These same researchers also examined the recoveries of Cereclor 42 and Chlorez 700 fortified on sediment to 463 and 277 µg/g on a wet weight basis, respectively. Extraction of wet spiked sediment with acetone or dimethyl formamide yielded no recovered chlorinated paraffins. However, elution of air-dried sediment with hexane provided nearly quantitative recovery. The amount of solvent required could be reduced by using 50% ether.

In summary, analytical procedures for detecting trace amounts of chlorinated paraffins are not anywhere near as sensitive or specific as techniques commonly used with organochlorine pesticides. The microcoulometric-gas chromatographic technique using petroleum ether extraction, acetonitrile partitioning, and U.V. irradiation cleanup (Friedman and Lombardo, 1975) seems to be the most specific and sensitive, but can only be used with the shorter chain (C_9 - C_{17}) chlorinated paraffins. The procedure is capable of measuring levels of at least 0.5 ppm in fish flesh (Lombardo et al., 1975). The application of this technique to biological or other environmental samples requires a great deal of caution since the specificity of the method is based on gas chromatographic peak pattern recognition. Lombardo et al. (1975) have demonstrated, at

least with Chlorowax 500 C accumulated in fish, that the pattern of peaks can change considerably due to selective uptake or differential metabolism and/or elimination.

For the longer chain (C_{20} - C_{25} formulations, the procedure used by Zitko (1973) appears to be the most sensitive (sensitivity 2 ng of chloride-measured down to 1 µg/g wet weight of fish food), but very unspecific. The procedure consisted of hexane extraction, alumina chromatographic column cleanup (remove lipids), silica column cleanup (remove PCB's), followed by direct microcoulometric quantitation (20 w/v% DEHP or Nujol in hexane solution for injection). The lack of specificity limits any application of this technique to environmental samples. Unfortunately, the confirmatory test suggested by Zitko (1974b) requires high concentrations of the chlorinated paraffin (limit of detection - 25 mg/g of lipid) and relies on gas chromatographic peak pattern recognition of the paraffin hydrocarbon (selective degradation, uptake, metabolism, or elimination may obscure the pattern).

2. Monitoring

No published monitoring information on chlorinated paraffins in environmental samples has been noted in the United States. However, communication with Beynon (1975), indicates that some monitoring data for Great Britain is about to be published and that additional information is being developed. The details of the information were not available in time for inclusion in this report, but should be published in a few months.

Zitko (1973) has noted a discrepancy between the total chlorine in herring gull yolk, seal blubber, and fish food and the chlorine that can be accounted for by PCB's or DDT and metabolites, even after alumina column cleanup with hexane solvent (see Table 29, p. 70).

III. Health and Environmental Effects

A. Environmental Effects

1. Persistence

Chlorinated paraffins placed in the environment may degrade by one of the following processes: (a) biodegradation - effected by living organisms, (b) photochemical degradation - non-metabolic degradation requiring light energy, and (c) chemical degradation - non-metabolic degradation catalyzed or effected by ubiquitous substances, such as oxygen, water, soil, etc. This section is devoted to biological and chemical degradation of chlorinated paraffins in the environment; the available information on photochemical reactions has already been discussed in Section I-B-4, p. 18.

a. Biological Degradation, Organisms, and Products

Chlorinated paraffins have not been extensively investigated for their environmental fate. Research along these lines has been hampered by the complex nature of the commercial preparations of chlorinated paraffins, which makes interpretation of the biodegradation data and identification of breakdown products extremely difficult.

The salient features of the available microbial degradation studies with commercial preparations of chlorinated paraffins are summarized in Table 31. Hildebrecht (1972) conducted a preliminary study to determine the biodegradability of samples of various chlorinated waxes containing small proportions of surfactant (formulations supplied by Diamond Shamrock Chemical Corporation) (see Table 31). Biochemical oxygen demand (BOD) was measured

Table 31. Summary of the Biodegradation Studies With Commercial Preparations of Chlorinated Paraffins

Reference	Commercial Preparations Studied	Concn. Used	Type of Micro-organisms Employed	Duration of the Test	Criteria for Test Chemical Alteration	Remarks
	Diamond Shamrock products					
Hildebrecht (1972)	A Chlorowax 500C 75% Surfactant 5% Water 20%	500 ppm	Sewage seed acclimated to increasing concentrations of chlorinated waxes up to 100 ppm	5 days for BOD test; 20 hrs. for Warburg respirometer	Oxygen uptake	The author assumed that oxygen consumption >35% of the theoretical implies that the compound is biodegradable. The validity in the assumption is questionable.
	B Chlorowax 40 75% Surfactant 5% Water 20%					
	C Chlorowax 70 37.5% Perchloroethylene 37.5% Surfactant 5% Water 20%					
	D Exchlor SC 75% Surfactant 2.5% Water 22.5%					
	E Concentrated surfactant-rated as 100% biodegradable					
Zitko and Arsenault (1974, 1975)	Cereclor 42 (ICI, 42% chlorine)	463 µg/g sediment	Estuarine sediments	30 days	Loss of parent compound	Analysis by direct injection microcoulometry of the hexane extract of dried soil
	Chlorez 700 (Dover, 70% chlorine)	277 µg/g sediment				

by Warburg respirometry and by the dilution method. In each method, the bacterial seed was acclimated to the individual chlorinated paraffin formulation before the test was run. The results of this investigation are presented in Table 32. Interpretation of the results of the test is somewhat difficult in view of the shortcomings discussed below.

The measurement of oxygen consumption can provide an estimate of the extent of biodegradation, when compared to data on the theoretical oxygen demand (TOD). Hildebrecht (1972) attempted to calculate the TOD from the measured total organic carbon (TOC). However, since the oxygen is consumed in producing carbon dioxide from the available carbon as well as water from the available hydrogen, the TOD calculated in this fashion will only be approximate. On the other hand, if one assumes that all the chlorine and hydrogen available in chlorinated paraffins is consumed in the production of hydrogen chloride, the calculated TOD would be approximately correct. This difficulty in the derivation of the TOD values makes the experimental results somewhat difficult to interpret. Furthermore, Hildebrecht (1972) uses arbitrary criteria for defining biodegradability; he defines anything that consumes greater than 35% TOD as biodegradable. The validity of this assumption is particularly doubtful when chemical mixtures are studied; 35% oxygen consumption can be obtained merely if one component of the mixture (which may amount to 35% of the total carbon) is completely degraded to carbon dioxide. Another difficulty encountered in interpretation of the data is that the author adds unspecified "bionutrients" during the acclimation phase and during the oxygen consumption test. If these are inorganic nutrients, they probably have little effect on the test results. However, if organic materials are included, they can have considerable impact on the interpretation of the results. For instance, nutrients may be oxidized along with the test chemical thus complexing the BOD results.

Table 32. Oxygen Consumed in BOD Bottle Test and Warburg Respirometer with Chlorowaxes (Hildebrecht, 1972)

Commercial Preparations Studied (see details in Table 31)	Biological Oxygen Demand			
	Respirometry (20 hrs)		Dilution Method (5 days)	
	Oxygen Consumed (mgs/l)	% of Theoretrical oxygen demand*	Measured BOD (mg/l)	% of Theoretical Oxygen Demand*
A	484	40	470	39
B	83	17.2	120	25
C	298	17.2	30	2
D	279	17.2	50	3
E	377	46.5	530	65

*The author has based his calculation of theoretical oxygen demand on the total carbon content of the sample and not on the empirical formula.

In view of the shortcomings in this study, only qualitative conclusions seem justified. The Chlorowax 500C seems to be degraded to some extent by microorganisms. The other Chlorowax formulations are much more stable in the Warburg test, although Chlorowax 40 appears to degrade somewhat under the dilution BOD bottle conditions. The degradation products that may be formed could not be determined by this method.

Zitko and Arsenault (1974, 1975) have studied the biodegradation of commercial chlorinated paraffins (Cereclor 42 and Chlorez 700) in estuarine sediments under anaerobic and aerobic conditions. The test mixtures were made by charging 25 g of previously spiked sediment, 300 mℓ of sea water, and 10 mℓ of a suspension of decomposing organic matter in sea water to a 500 mℓ Erlenmeyer flask. The aerobic flasks were aerated while the anaerobic flasks

were kept stoppered. After various periods of incubation, the concentration of chlorinated paraffins in the sediment was determined by air-drying a sample of sediment followed by hexane-ether (50/50) extraction and direct injection microcoulometric quantitation. Some of the controls contained microcoulometrically active interferences. The results are presented in Table 33.

Table 33. Biodegradation of Chlorinated Paraffins in Spiked Sediments (Zitko and Arsenault, 1974, 1975)

Time (days)	Concentration in Sediment, μg apparent chlorine/g of Sediment, dry weight			
	Aerobic		Anaerobic	
	Cereclor 42	Chlorez 700	Cereclor 42	Chlorez 700
0	596	357	596	357
10	257	76	80	41
21	147	128	194	33
28	377	72	98	50

In addition, thin-layer chromatography and IR spectrophotometry on hexane/ether extracts of the remaining sediment dried in vacuum were also used to follow the loss of chlorinated paraffins. Only traces of the chlorinated paraffins were found after 30 days of incubation.

Zitko and Arsenault (1974, 1975) concluded that the chlorinated paraffins are biodegradable in sediment and that the rate was higher under anaerobic conditions. However, the reproducibility of the latter conclusion is questionable considering the inconsistency of the general trends in Table 33. For example, under aerobic conditions with Cereclor 42, more apparent chlorine is detected at 28 days than at 10 or 21 days. Zitko and Arsenault (1974) also pointed out that the analytical procedures used would not allow for the measurement of more polar, chlorine-containing transformation products that might be formed. Thus, the actual mineralization of chlorinated paraffins (conversion to chloride) may be much less than indicated from the experimental data.

Overall, the results of the studies concerning the environmental biodegradability of chlorinated paraffins are inconclusive. Studies of Zitko and Arsenault (1974, 1975) have shown that the detectable amount of Cereclor 42 and Chlorez 700 in sediment decreases with time; however, the extent of degradation of these compounds is uncertain. Of the Chlorowax formulations, only Chlorowax 500C and perhaps Chlorowax 40 appear to be biodegradable to some extent (Hildebrecht, 1972). No information is available on the products of biodegradation.

b. Chemical Degradation in the Environment

The available information on the chemical reactivity of chlorinated paraffins has already been reviewed in Section I-B, p. 16. The information presented there would suggest that chlorinated paraffins do not hydrolyze, oxidize, or otherwise react at significant rates under ambient temperature and relatively neutral conditions. Thus, it would appear that these compounds are fairly chemically stable under environmental conditions. Their use in applications which require chemical resistance, such as traffic and marine paints, lends support to this conclusion. However, the chlorinated paraffins can be catalytically dehydrochlorinated in the presence of iron oxides as well as other inorganic compounds, and the possibility of this process occurring in nature seems quite feasible. Unfortunately, no experimental data are available on the chemical stability of chlorinated paraffins under simulated environmental conditions.

2. Environmental Transport

Transport of chemicals in the environment depends upon such physical processes as adsorption on colloidal substances, volatilization,

bioaccumulation and leaching. These processes result in distribution and dilution, or concentration, of contaminants. Although no experimental data are reported in the literature, an attempt has been made in this section to look at environmental movement of chlorinated paraffins based on their physical properties.

Considering the low solubility of normal C_{10} - C_{30} paraffins in water, and the increasing hydrophobic effect of chlorine substitution, it appears likely that chlorinated paraffins are insoluble in water and adsorb readily on suspended particles. A tight binding of chlorinated paraffins to estuarine sediment is suggested from the fact that Zitko and Arsenault (1974) failed to extract chlorinated paraffins from wet spiked sediment with such polar solvents as acetone or dimethyl formamide. This low water solubility and tight binding to sediment would suggest that chlorinated paraffins probably are not leached through soils at appreciable rates.

Most commercially available chlorinated paraffin preparations are non-volatile at temperatures around 20°C (volatility generally $< 6 \times 10^{-4}$ gms/cm^2/hr at 100°C. The measured vapor pressure of a $C_{23}H_{48}$, 42% - 54% Cl, chlorinated paraffin is reported to be 2×10^{-5} mm Hg, which is similar to PCB's (see Table 23, p. 51). Thus, because of the low vapor pressure and low thermal stability (destroyed before volatilized), evaporation and atmospheric transport probably have a very small role in the distribution of chlorinated paraffins in the environment.

Chemicals in aquatic systems can be lost to the atmosphere by co-distillation with water. However, in view of the high molecular weight of chlorinated paraffins, and the fact that in aquatic systems, these materials will be adsorbed on the suspended matter, it seems unlikely that these chemicals will be lost to the atmosphere to a significant extent by co-distillation from water.

3. Bioaccumulation

In view of the high molecular weight of chlorinated paraffins, their bioaccumulation potential appears to be limited. The ability of chlorinated paraffins to strongly adsorb to suspended particulates in water will further reduce their availability to food chain organisms. Zitko (1974a) has studied the uptake of chlorinated paraffins (Cereclor 42, and Chlorez 700) by juvenile Atlantic salmon (Salmo salar). Chlorinated paraffins were administered: (a) adsorbed on suspended solids simulated by silica, and (b) in food. The results of this study using both administration methods are presented in Table 34.

Table 34. Uptake of Chlorinated Paraffins and PCB from Suspended Solids and Food by Juvenile Atlantic Salmon (Zitko, 1974a)

- In Suspended Solids -

Preparation	Time of exposure, hr.	Concentration in Fish: Chlorine µg/g wet wt.	µg PCB or Chlorinated Paraffin/g wet wt.	Lipid %
Control	48	0.34		0.99
Cereclor 42	48	0.44	1.05	1.10
	144	0.75	1.79	1.33
Chlorez 700	48	0.22	0.31	1.56
	144	0.46	0.66	2.10
Aroclor 1254	24		19.9	1.52
	48		28.3	1.86
	144		134	1.78

-In Food-

Days of Feeding	33		109		181	
Diet	Residue*	Lipid%	Residue*	Lipid%	Residue*	Lipid%
Control	0.30	1.03	nd+	0.65	nd+	0.47
Cereclor 42, 10 µg/g	0.11	1.30	nd	0.69	nd	0.49
100 µg/g	0.51	1.22	nd	0.49	nd	0.34
Chlorez 700, 10 µg/g	0.29	1.13	nd	0.40	nd	0.29
100 µg/g	0.49	1.30	nd	0.56	nd	0.92
Aroclor 1254, 10 µg/g	3.86**	5.09	3.80**	3.10	3.80**	2.07
100 µg/g	13.9**	5.30	24.0**	2.73	30.0**	2.69

* Expressed as chlorine, µg/g wet weight
** Expreseed as Aroclor 1254
+ Not detectable, < 0.05 µg/g

Although somewhat inconclusive, the results suggest that chlorinated paraffins do not accumulate in significant quantities in juvenile Atlantic salmon under either of the experimental conditions employed. Since the analytical method used measured chlorine and not chlorinated paraffins, it is uncertain if the levels of chlorine detected were due to chlorinated paraffins. Under similar conditions, polychlorinated biphenyls, which were used for comparison, were found to bioaccumulate to a much greater extent. Since high levels of chlorine were not detected when chlorinated paraffins were used, it was concluded that these compounds do not bioaccumulate.

Lombardo et al. (1975) fed fingerling rainbow trout a diet fortified with 10 ppm of Chlorowax 500C. Because Chlorowax 500C contains much lower molecular weight isomers than the chlorinated paraffins studied by Zitko (1974a), microcoulometric gas chromatography (with ultraviolet irradiation cleanup - see Section II-E, p. 62) was used for analysis. Samples were taken at 2 week intervals over an 82 day period, and chlorinated paraffin residues of as high as 1.1 ppm on a tissue basis, or 11-18 ppm on a fat basis, were found. Because of an early termination of the study, Lombardo and coworkers (1975) were unsure whether an equilibrium level had been reached. However, the low levels found using a much more specific analytical technique tend to confirm the conclusion of Zitko (1974a) that chlorinated paraffins bioaccumulate much less than PCB's. The study by Lombardo et al. (1975) also demonstrated that bioaccumulation rates for different isomers in the Chlorowax 500C formulation are quite different (major differences in the intensities of the GLC peaks). The authors attributed this difference to differential uptake, metabolism and/or elimination.

4. Biomagnification

Biomagnification refers to concentration of a compound through the consumption of lower organisms by higher food chain organisms with a net increase in tissue concentration (Isensee et al., 1973). Although the biomagnification potential of chlorinated paraffins has not been studied as such, some inferences regarding its biomagnification potential can be drawn from the studies of Zitko (1974a) and Lombardo et al. (1975) which deal with the accumulation of chlorinated paraffins in fish fed chlorinated paraffin contaminated food. Since the fish in these studies failed to accumulate significant quantities of chlorinated paraffins from synthetic fish food containing chlorinated paraffins (see Section III-A-3, p. 82), it appears unlikely that considerable increases in tissue chlorinated paraffin concentrations will occur through consumption of lower food chain organisms. However, a different conclusion can be reached by considering the solubility characteristics of chlorinated paraffins. Based on the solubility of parent hydrocarbons and solubility decreasing effect of chlorine substitution, Zitko and Arsenault (1974) have predicted that chlorinated paraffins will be less soluble than PCB's in water. Metcalf and Lu (1973) have determined the ecological magnification ($\frac{\text{concentration in organism}}{\text{concentration in water}}$) for PCB's in a model ecosystem; it was found to be in the range of 6500-12000 for fish and 6000-60,000 for snails. Since ecological magnification in the model ecosystem has been found to increase with an increase in water insolubility (Metcalf and Lu, 1973), the ecological magnification for chlorinated paraffins would be suspected to be greater than for PCB's; a conclusion which is not supported from the experimental data (see Zitko 1974a; Lombardo et al., 1975). The inability of chlorinated

paraffins to accumulate and biomagnify could be attributed to their higher molecular weight; the bulkiness of the molecules may prevent them from being taken up by the living organisms.

Although a number of vital questions concerning bioaccumulation and biomagnification potential of chlorinated paraffins remain unanswered, the information available tends to suggest that significant bioaccumulation and biomagnification of the unaltered chlorinated paraffins in the food chain will not occur.

B. Biology

Foreign compound absorption, distribution, biotransformation, and excretion are intimately connected processes in living organisms. The ultimate physiological action of an administered substance will be determined not only by the extent to which it is absorbed into the systemic circulation, but also by the form in which it arrives. Extensive transformation prior to absorption is often catalyzed by enzymes of the liver and other tissues, or may result from the action of gut flora and gastric secretions. The consequences of different routes of administration can result in extreme variation in the biological activity of a single compound, based on the sequence of organ systems through which the substance passes.

1. Absorption

Digestive absorption of chlorinated paraffins in juvenile Atlantic salmon could not be demonstrated either by feeding concentrations of 10 and 100 ppm of Cereclor 42 (42% chlorine) or Chlorez 700 (70% chlorine) in the diet for 181 days, or by exposing fish to these compounds adsorbed on silica (Zitko, 1974a). In contrast, a PCB preparation, Aroclor 1254, was readily absorbed under similar conditions (Zitko and Hutzinger, 1972) (for comparison, see Section III-A-3, p. 82). Chlorinated paraffin levels were determined by the measurement of chlorine obtained by passing tissue extracts directly into a microcoulometric detector (see Section II-E-1, p. 62). Unfortunately, the method is not specific for chlorinated paraffins but adequately demonstrates that very little adsorption occurs. Zitko (1974a) noted that the high molecular weight of chlorinated paraffins may slow down or inhibit their digestive absorption, which was shown to be the case with normal paraffins (Zitko and

Arsenault, 1974). The possible absorption of biotransformation products or fragmented short-chain hydrocarbon impurities was not determined.

Lombardo et al. (1975) reported that fingerling rainbow trout fed 10 ppm of Chlorowax 500C (59% chlorine) in the diet for up to 82 days slowly accumulated chlorinated paraffin residues in their tissues. Chromatographic evidence (microcoulometric detection) indicated that a differential absorption or metabolic transformation of the Chlorowax 500C occurred, based on a comparison of tissue residues to the parent compound in spiked controls. Further investigations to determine the extent of chlorinated paraffin absorption in higher animals by either dermal, oral or parenteral routes have not been encountered in the literature.

2. Excretion

No data are available.

3. Transport and distribution in living organisms

No data are available.

4. Metabolic effects

No data are available.

5. Pharmacology

No data are available.

C. Toxicity - Humans

The approach to human toxicity must take into consideration the exact nature of a particular compound or commercial product to which man is exposed. It has been noted that various commercial preparations of chlorinated paraffins may vary significantly with respect to the presence of manufacturing impurities in the finished product (Diamond Shamrock Chemical Company, 1975). Unfortunately, detailed information on identity or toxicity is not available for the chlorinated acyclic or aromatic hydrocarbons

which may be present as impurities in chlorinated paraffins (see Section I-A-3, p. 12). In addition, low molecular weight chlorinated hydrocarbon fragments known to result from the decomposition of chlorinated paraffins may represent a potential hazard in view of the well-known carcinogenic effects of vinyl chloride (Zitko and Arsenault, 1974).

1. Controlled Studies

The toxic hazards associated with acute exposure to chlorinated paraffins appear to be relatively low based on the limited data which are presently available. This observation is supported by the fact that no cases of industrial poisoning or contact dermatitis have been reported in workers involved in the production and handling of these compounds.

Reports supplied by Dover Chemical Corporation (1975a) indicate that Paroil 142 (40-41% chlorine) and Chlorez 700 (70% chlorine) were not active as primary local irritants when applied as patches to the skin of two hundred male and female volunteers for a five day period. Reapplication of the material for two days beginning three weeks after the initial exposure produced no allergic or other toxic responses. Similar studies have been reported by Diamond Shamrock Chem. Co. (1975) indicating that Chlorowax 70 (70% chlorine), Chlorowax 500C (59% chlorine) and Chlorowax 40 (43% chlorine) did not produce local irritation or allergic responses when applied to the skin of two hundred male and female subjects. The period of exposure and amount of chlorinated paraffin product used in these studies are not known. Results of the above studies indicate that selected chlorinated paraffin products when applied dermally do not stimulate a cell-mediated immune response or produce delayed hypersensitivity

reactions. It has not been established, however, whether the dose of chlorinated paraffin employed may have been below the threshold concentration required for sensitization, as has been demonstrated with known contact allergens (Rostenberg and Kanof, 1941).

2. Epidemiology

No data are available.

3. Occupational Studies

No data are available.

D. Toxicity - Birds and Mammals

Animal studies on the effects of chlorinated paraffin administration have been limited to the observation of gross toxicological responses to acute oral and dermal exposures. Chronic and acute studies have not been encountered which report hematological, gastro-intestinal, or neurological measurements, nor have the effects of parenteral administration of chlorinated paraffins been investigated.

1. Acute (Table 35)

Single dose oral ingestion of Chlorowax 70 at 50 g/kg in rats and 25 g/kg in guinea pigs produced no mortalities (Diamond Shamrock Chem. Co., 1975). Similarly, death did not result from the feeding of Chlorowax 40 at 10 ml/kg in male rats. The oral LD_{50} of Chlorowax 500C in rats is greater than 21.5 ml/kg of body weight. In tests reported by Dover Chemical Corporation (1975b), rats given oral doses of 10-50 g/kg of Chlorez 700 all survived a two week observation period, although a 20% mortality occurred at the 60 g/kg dosage, presumably due to mechanical injury. Guinea pigs given oral doses of 5-25 g/kg of Chlorez 700 all survived a two-week observation, whereas a 40% mortality resulted in those animals fed 30 g/kg of body weight.

Table 35. Summary of Acute Animal Toxicity of Chlorinated Paraffins

Species	Compound	Dose (g/kg)	Route of Administration	Exposure Period	Effects	Reference
Rat	Chlorowax 70	50.0	Oral	Single Dose	No Mortality	Diamond Shamrock Chem. Co., 1975
Guinea Pig	Chlorowax 70	25.0	Oral	Single Dose	No Mortality	Diamond Shamrock Chem. Co., 1975
Rat	Chlorowax 40	10 ml/kg	Oral	Single Dose	No Mortality	Diamond Shamrock Chem. Co., 1975
Rat	Chlorowax 500C	0.464-21.4 ml/kg	Oral	Single Dose	14 day observation; LD_{50} > 21.5 ml/kg	Diamond Shamrock Chem. Co., 1975
Rat	Chlorez 700	10.0 - 50.0	Oral	Single Dose	All survived a two week observation period	Dover Chemical Corp. 1975b
Rat	Chlorez 700	60.0	Oral	Single Dose	20% mortality due to mechanical injury	Dover Chemical Corp. 1975b
Guinea Pig	Chlorez 700	5.0 - 25.0	Oral	Single Dose	All survived a two week observation period	Dover Chemical Corp. 1975b
Guinea Pig	Chlorez 700	30.0	Oral	Single Dose	40% mortality due to mechanical injury	Dover Chemical Corp. 1975b
Rabbit	Chlorowax 500C	1.0-10 ml/kg	Dermal-occluded	24 hours	14 day observation; LD_{50}> 10 ml/kg	Diamond Shamrock Chem. Co., 1975
Rabbit	Chlorowax 500C	?	Topical (eye)	?	Mild erythema in 4 of 6 test animals	Diamond Shamrock Chem. Co., 1975
Rat	Chlorowax 500C	3.3 mg/l	Inhalation	One hour	None observed	Diamond Shamrock Chem. Co., 1975
Mouse	KhP 470	21.85 + 24.0	Oral	Single Dose	LD_{50} at 21.85 g/kg and LD_{100} at 24.0 g/kg	Abasov, 1970
Rat	KhP 470	26.1 + 28.0	Oral	Single Dose	LD_{50} at 26.1 g/kg and LD_{100} at 28.0 g/kg	Abasov, 1970

The dermal LD_{50} in rabbits for Chlorowax 500C was reported to be greater than 10 ml/kg of body weight (Diamond Shamrock Chem. Co., 1975). In the same study, a single application of Chlorowax 500C to the eyes of rabbits produced a mild erythema in four of six test animals. Inhalation toxicity was not encountered in rats exposed to an air concentration of 3.3 mg/l of Chlorowax 500C for a one hour period.

In studies conducted by Abasov (1970) with chlorinated paraffin KhP-470, an abstract of the original article states that a single oral dose to mice resulted in death at a minimum concentration of 19 g/kg, with the LD_{50} and LD_{100} being 21.85 and 24.0 g/kg of body weight, respectively. When administered to rats, mortality was evident at 24.5 g/kg and the LD_{50} and LD_{100} were 26.1, and 28.0 g/kg, respectively. Although KhP-470 demonstrated no effect when applied to skin, conjunctivitis resulted from contact with the mucous membrane of the eye of test animals. While the lethality of KhP-470 appears to exceed that of other commercial preparations, data are not available concerning the formulation and chlorine content of this product, thereby making direct comparison impossible.

2. Subacute

   No data are available.

3. Sensitization

   No data are available.

4. Teratogenicity

   No data are available.

5. Mutagenicity

   No data are available.

6. Carcinogenicity

No data are available.

7. Chronic Studies

No data are available.

8. Behavioral Effects

No data are available.

9. Possible Synergisms

No data are available.

E. Toxicity - Lower Animals

In a recent report on the accumulation of chlorinated paraffins in juvenile Atlantic salmon, Zitko (1974a) demonstrated an insignificant uptake of Cereclor 42 and Chlorez 700 when fish were exposed to these compounds at levels of 10 and 100 ppm in the diet for an extended period. Mortality was evident, however, among those fed the chlorinated paraffin contaminated diet. An LT_{50} (number of days to reach 50% mortality) ranging from 39-80 days was noted, as opposed to the control group with an LT_{50} of 138 days. A determination was not possible of the actual amount of food consumed by the fish in this experiment, and consequently, the daily dose of chlorinated paraffin ingested could not be calculated. In a similar study by Lombardo et al. (1975), fingerling rainbow trout were fed a diet containing 10 ppm of Chlorowax 500C for up to 82 days. Gross toxicological effects were not evident in treated fish although their increase in average body weight throughout the experiment was consistently less than the control group.

Additional data supplied by Johnson (1975) and summarized in Table 36 demonstrate that LD_{50} values for various Chlorowax preparations against bluegills and rainbow trout were consistently greater than 300 mg/l under standard static toxicity test conditions. Variations in test temperature between 5 and 25° did not alter the static toxicity of Chlorowax 500C.

Table 36: Acute Fish Toxicity of Chlorowax Preparations (Johnson, 1975)

SPECIES	COMPOUND	SIZE (g)	TEMP. (c)	96 hr. LC 50 (mg/ℓ)
Rainbow trout	Chlorowax 40	0.7	10	>300
Bluegill	Chlorowax 40	0.5	20	>300
Rainbow trout	Chlorowax 50	0.7	10	>300
Bluegill	Chlorowax 50	0.5	20	>300
Rainbow trout	Chlorowax 70	0.7	10	>300
Bluegill	Chlorowax 70	0.5	20	>300
Rainbow trout	Chlorowax 500C	0.5	10	>300
Fathead minnow	Chlorowax 500C	0.8	20	>100
Channel catfish	Chlorowax 500C	1.1	20	>300
Bluegill	Chlorowax 500C	0.7	20	>300
Rainbow trout	Chlorowax LV	0.7	10	>300
Bluegill	Chlorowax LV	0.5	20	>300

In a flow-through test system, LC_{50} values obtained for bluegills and channel catfish were greater than 100 mg/l after 13 days exposure, and likewise for rainbow trout after 24 days. Various sub-lethal effects, however, were noted in the flow-through tests with rainbow trout at concentrations down to 40 µg/l. These effects were manifested as a progressive loss of motor function leading to immobilization beginning within 15 to 20 days. Where death occurred, it resulted from debilitation, cessation of feeding, and other secondary effects. Differences in susceptibility could not be demonstrated among rainbow trout yolk-sac fry, swim-up fry, and fingerlings. Bluegills and channel catfish did not generally exhibit these sub-lethal effects.

F. Toxicity - Plants

No data are available.

G. Toxicity - Microorganisms

Very little work has been done concerning the toxicity of commercial chlorinated paraffins to microorganisms. Hildebrecht (1972) investigated the effect of Chlorowaxes (Chlorowax 500C, Chlorowax 40, Chlorowax 70 and Exchlor SC) on oxidative metabolism of sewage seed employing potassium acid phthalate, a readily biodegradable substance, as substrate. Bottles containing an exact amount of potassium acid phthalate, bionutrients, and bacteria seed were incubated for five days and served as controls. The average residual dissolved oxygen at the end of the incubation period was found to be 4.6 mg/l. When chlorinated paraffins were added to the system at concentrations of 1.0, 10, 50, 100, and 200 mg/l, the residual dissolved oxygen values after five days incubation were all less than 1.0 mg/l. These results indicated that chlorinated paraffins were not toxic enough to alter the oxidizing ability of the bacteria since the utilization of oxygen was not inhibited, as evidenced by the decreased dissolved oxygen at the conclusion of the test.

H. Effects on inanimate objects and structures

No data are available.

IV. Regulation and Standards

A. Current Regulation

According to the definitions and regulations as outlined in the Federal Register of August 12, 1961, the chlorinated paraffins which have thus far been tested for toxicity do not classify as hazardous substances. The Commissioner of Food and Drugs has concluded that for a substance to be considered toxic by oral ingestion it must produce death within 14 days in one-half of a group of adult rats at a single dose of 0.050-5.0 grams per kilogram of body weight. Similarly, for dermal toxicity in rabbits, an LD_{50} must be achieved at doses between 0.2 and 2.0 grams per kilogram of body weight. For inhalation toxicity in rats, an atmospheric concentration of 2.0-200 milligrams of foreign substance per liter of air must produce 50% mortality. The data which are summarized in Table 35 indicate that none of the commercial chlorinated paraffin products tested produced lethal effects at levels below the maximum dose for toxicity as specified in the federal regulations. In addition, the Food and Drug Administration has amended the food additive regulations to provide for the use of "chlorinated liquid n-paraffins with chain lengths of C_{10} - C_{17} containing 40-70% percent chlorine by weight" as components of food-packaging adhesives (Anon., 1969). Under this regulation, the contact of these substances with fatty and aqueous foods is limited to trace amounts at package seams and edges of packaging laminates. For dry foods, packaging adhesive contact is limited by the standards of "good manufacturing practice." Chlorinated paraffins alone have not received approval for direct contact with foods as regulated under Federal Code 21 CFR 121.2526.

B. Consensus and Similar Standards

The chlorinated paraffins are rated as Class I, "practically non-toxic" in "Clinical Toxicology of Commercial Products" (Gleason, 1969). This source states that injury in test animals did not occur short of doses which produced intestinal obstruction. Furthermore, a calculated probable lethal dose in humans was given as greater than 15 grams per kilogram of body weight or more than one quart for a 70 kilogram man.

The American Conference of Governmental Industrial Hygienists, which assigns threshold limit values to most toxic substances in workroom air does not list chlorinated paraffins in its compendium.

The 1974 edition of the "Toxic Substances List" was prepared by the National Institute for Occupational Safety and Health to identify all known toxic substances, and contains some 13,000 unique chemical names. The chlorinated paraffins are not included in the list, although this may be due to insufficient data concerning dosage/effect relationships.

V. Summary and Conclusions

Commercial chlorinated paraffins are extremely complex mixtures of isomers and analogs of compounds formed when mixtures of n-paraffins (C_{10}- C_{30}) are chlorinated to varying percentages of chlorine (usually 40-70% by weight). Both liquid products (40-64% chlorine) and solid resins (∿70% chlorine) are commercially available.

In 1973, 74 million pounds of chlorinated paraffins were produced in the United States by eight manufacturers with plants located at ten different geographic locations. The product is formed by liquid phase chlorination of the warmed paraffin feed stock using either batch or continuous reactors. The free-radical chlorination can be catalyzed by UV light, and the by-product hydrogen chloride and residue chlorine are removed by blowing air through the product. With the resinous products (∿70% chlorine), a solvent such as carbon tetrachloride is used to increase the viscosity and chlorination rate.

Major applications of chlorinated paraffins include uses as lubricating oil additives (45% of total production), secondary vinyl plasticizers (24%), flame retardants in rubber, plastics, and paints (27%), and traffic paint additives (4%). Information on the quantities used in the various applications is somewhat contradictory and could use some clarification. The viscosity of the liquid formulations and the ability to slowly release hydrogen chloride at elevated temperatures allows the chlorinated paraffins to be used as boundary and extreme pressure lubricant additives. Chlorinated paraffins are used as secondary plasticizers, mostly in polyvinyl chloride (PVC), to reduce the cost and maintain the flame retardancy of the resin. Other plasticizers, such as diethylhexyl phthalate, increase the flammability of the final product, and conventional flame

retardant plasticizers, such as organophosphate esters, cause poor low temperature properties for the resin. Chlorinated paraffins can be used as flame retardants because they degrade at elevated temperatures to yield hydrogen chloride, which is effective in retarding combustion. Sizable quantities of chlorinated paraffins are also used in chemically resistant paints, such as traffic and marine paints. The chlorinated paraffins have also been suggested as Aroclor (PCB's) replacements, especially in rubber-based paints and adhesives. These markets for chlorinated paraffins (especially the flame retardant applications) will likely continue to grow at appreciable rates (oil additives, ~5%/year; others, 10-35%/year).

No published field monitoring data are available on the amounts of chlorinated paraffins that are released to and accumulate in the environment, although some monitoring data for Great Britain should be available shortly. Much of this paucity of information is attributable to the lack of specific and sensitive analytical methods. Gas chromatography using electron capture detection or combined with mass spectrometry has been evaluated and considered unacceptable for chlorinated paraffins. With the shorter chained (C_9 - C_{17}) chlorinated paraffins, where the compounds are volatile enough to pass through a gas chromatographic column, a relatively specific microcoulometric-gas chromatographic technique has been devised that is capable of measuring 0.5 ppm in fish flesh. With the higher chained (C_{20} - C_{30}) chlorinated paraffins, only the very non-specific direct injection microcoulometric detection method has been used at 1 ppm concentrations. Neither of these methods is capable of measuring chlorinated paraffins at background environmental levels. It has been suggested that a combination of liquid chromatography with microcoulometric detection would be a very appropriate system for analyzing trace amounts of chlorinated paraffins.

Although there is no conclusive evidence that chlorinated paraffins are released into the environment, many of their applications are identical to the ones suspected as being the major source of polychlorinated biphenyl (PCB) contamination. Release of chlorinated paraffins used as oil additives to water resources and landfills is probably very sizable, since waste oil is frequently not recovered and this application is a major market for chlorinated paraffins. Chlorinated paraffins may also reach the environment as plasticizers in plastics (discarded in solid waste), by leaching from traffic and other paints, and as components of materials that have chlorinated paraffins incorporated in them for flame retardancy (also discarded in solid waste). Some quantitative estimates of the losses were made in this report but were based only on speculation.

Only a limited number of studies have been conducted on the fate of chlorinated paraffins that might reach the environment. The biochemical oxygen demand for several Chlorowax formulations (aqueous suspensions) has been determined by the dilution bottle and Warburg technique. One of these formulations (Chlorowax 500C) seems to be relatively biodegradable based on oxygen consumption, but it is difficult to assess the extent of degradation or whether only selective isomers are being degraded. Loss of "apparent chlorine" content (direct injection microcoulometry) from both anaerobic and aerobic sediments that were spiked with chlorinated paraffins has been observed. However, no information is available on the structure of the degradation products and no radiolabelled studies have been reported.

The chlorinated paraffins that reach the environment are probably less mobile than PCB's. The chlorinated paraffins are less thermally stable than

PCB's and, therefore, are most likely destroyed rather than volatilized in conventional incineration processes. However, experimental data confirming this behavior is lacking. The water solubility of chlorinated paraffins has not been exactly measured, but is extremely low and is probably lower than PCB's based on molecular weight considerations. This could suggest that chlorinated paraffins will probably migrate very slowly through soil (leach from landfills). Experimental evidence is available demonstrating that the parent compounds (both lower and higher molecular weight formulations) are not bioaccumulated by juvenile Atlantic salmon or fingerling rainbow trout when the chlorinated paraffins are administered by adsorption on silica or by incorporation in the fish food. The possibility of the bioaccumulation of degradation products has not been studied.

Dermal application of chlorinated paraffins to human skin apparently does not produce local irritation or allergic sensitization. Furthermore, acute studies in non-human mammals have demonstrated that chlorinated paraffins possess extremely low toxicity when administered by oral, topical, and inhalation routes. Clearly lacking in the literature, however, are long term studies and investigations aimed at the determination of toxic reactions to chlorinated paraffin impurities and degradation products. Similarly, the question of biotransformation and metabolic activation of chlorinated paraffins into potentially harmful substances has not been answered as yet.

It is known, however, that the addition of chlorinated paraffins to the diet or in the water of various fish species will produce significant mortality and numerous sub-lethal effects. Further studies are indicated which should be designed to characterize and identify the mechanisms of action and true proximate substance involved in producing these toxic reactions.

Because the only toxicity thus far shown to result from exposure to chlorinated paraffins has involved subacute (>24 hrs.) administration in fish, it would seem worthwhile to explore possible subacute effects in higher animals. This type of study is particularly valuable since subacute administration more closely resembles environmental exposure. In addition, subacute exposure often involves different target organs than single dose treatments, and allows for the assessment of repeated damage to organs and organelles.

Thus, because of the limited data available, a conclusive environmental hazard assessment of chlorinated paraffins is not possible at this time. However, from the available information, it seems safe to state that the chlorinated paraffins pose less of an environmental hazard than PCB's at comparable contamination levels (a similar conclusion is reached by Zitko and Arsenault, 1974). Chlorinated paraffins are much less persistent, do not appear to bioaccumulate, and are less acutely toxic. However, there are considerable gaps in the available information. No published monitoring data are available yet; the chemical structure, bioaccumulation potential, and toxicity of the environmental degradation products are unknown; and the available toxicity data are completely inadequate for assessing possible detrimental effects from trace contamination. Sizable quantities of chlorinated paraffins are probably reaching the environment. Without the above- mentioned information, the hazard of environmental contamination by chlorinated paraffins cannot be fully evaluated.

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